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EFFECT OF VOLTAGE ON ODOUR AND SULPHIDE REMOVAL IN STORED PIG MANURE

BY

YINGHONG WANG

A thesis submitted to the **Faculty of Graduate Studies and Research** in partial fulfilment of the requirements for the degree of **MASTER OF SCIENCE.**

DEPARTMENT OF AGRICULTURAL ENGINEERING

EDMONTON, ALBERTA

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ISBN 0-612-11410-4

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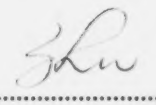

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ABSTRACT

Odours from stored liquid manure are the source of many complaints by adjacent land users. Oligolysis is an effective method for reducing odours although it is considered to be an expensive process. The objective of this experiment was to test the effects of voltage on the effectiveness of this process in the reduction of odour and sulphide in stored pig manure and to determine an optimum voltage. The experiment consisted of six treatments, with each treatment applied to two 0.225 m^3 bioreactors. Six treatment levels were 1.5, 2.0, 2.5, 3.0, 3.5 volts and a control (no voltage). Voltages were maintained by voltage regulators and monitored regularly. Each experiment occurred over a 15 day period and was repeated three times. Liquid samples were obtained at 0, 0.5, 3, 24 and 168 h. Gas samples were obtained at 0, 24 and 168 h.

The liquid samples were analyzed for free and total sulphide. The gas samples were analyzed for hydrogen sulphide (H_2S). A threshold odour number (T.O.N.) measurement was conducted by an odour panel on the liquid samples at 168 h.

The results indicate that the voltage treatments removed over 98% of the free sulphide in liquid pig manure. The mean concentration of H_2S in the gas released from the treated bioreactors was 91% lower than the control. No significant differences were observed among the applied voltage levels for all sulphide parameters measured. The dilution of manure for the T.O.N. test was 2.5 to 28.5

ppm of the original sample. No significant differences were observed among the treatments on T.O.N. although the odour of the undiluted treated manure appeared to be reduced.

ACKNOWLEDGEMENTS

My sincere appreciation goes to my supervisor Dr. J.J.R. Feddes for his guidance, supervision and continuous support throughout this program. I am grateful to Dr. R.N. Coleman and his staff at the Alberta Environmental Centre for their valuable advise and assistance. Special thanks to C. George for analyzing the samples.

Acknowledgement goes to the laboratory of the Department of Food Science for providing the odour free water and constant temperature water bath.

Further acknowledgement goes to the students in the Department of Agricultural Engineering for volunteering their time on the odour panel.

The advise provided by Dr. Hardin on data analysis also was much appreciated.

Thanks to my husband Hong Hao for his understanding, encouragement and support.

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1. INTRODUCTION

The predominant waste handling system for large-scale piggeries has become the liquid slurry system, i.e. pigs are kept on floors with slots, through which the deposited fecal material, urine, feed and water wastage drop into underlying storage pits. Handling and labour advantages are primarily responsible for this development. One of the problems arising with this storage system is the emission of nuisance odours and toxic gases because of the anaerobic degradation of the slurry. The odours from animal wastes are complex mixtures of malodorous gases and organic compounds. Hydrogen sulphide and sulphur containing compounds appear to be primary contributors. Hydrogen sulphide is not only odorous but highly toxic. There is conclusive evidence that H_2S is the main cause of poisoning, especially during agitation and pumping when the trapped gas is suddenly released. The problem has attracted the attention of many researchers and consequently a number of odour-abating and waste handling methods have been developed.

Oligolysis is an electrolytic treatment process in which two electrodes are immersed in slurry and a voltage is applied across the electrodes. The electric potential causes the anode to release metal ions into the slurry. These metal ions combine with sulphide ions (S^{2-}) that are available in the slurry forming metal sulphide precipitate which is insoluble. This prevents the S^{2-} from participating in other chemical reactions that may lead to the formation of odorous compounds such

as H_2S.

Oligolysis is an effective method in reducing the H_2S evolution and odour from anaerobic digestion of pig manure (Yu et al., 1990). With similar odour control, the energy requirement for oligolysis treatment can be 20-25 times lower than aeration treatment (Chiumenti et al., 1988). The process does not disturb the anaerobic digestion process in the stored pig manure.

Applied voltage was considered to be one of the important parameters affecting the oligolysis process. The voltage required for the oligolysis is dependent on the electronegative potential required for the oxidation of iron, electrical conductivity of the slurry, the electrode area and spacing of electrodes (Feddes, 1991).

The goal of this project was to evaluate the effect of voltage on the effectiveness of oligolysis treatment on odour and sulphide removal in stored pig manure by both chemical analysis and T.O.N. technique.

2. LITERATURE REVIEW

Biological breakdown of wastes occurs by both aerobic and anaerobic decomposition. Aerobic decomposition takes place when organisms have free oxygen (molecular or dissolved) present in their environment for their metabolic processes. Anaerobic organisms do not require free oxygen for metabolism, and in the presence of free oxygen their activity becomes significantly reduced. Anaerobes derive their oxygen from the compounds that they decompose.

The end products of the two decomposition processes are quite different. Aerobic decomposition reduces animal wastes to organic compounds of a simpler, less objectionable state, carbon dioxide (CO_2) and water (H_2O). In addition to simple organic compounds, H_2O and CO_2, anaerobic decomposition produces gases such as methane (CH_4), H_2S and ammonia (NH_3) which give rise to odour and may cause health impairment and death to livestock and humans when present in sufficiently high concentrations as could occur in enclosed environments.

Manure is generally stored as a liquid slurry because of ease of handling and reduction in labour. Under these conditions, degradation of slurry is normally anaerobic.

2.1 Processes in anaerobic treatment

The anaerobic treatment of wastes can be considered as a two stage process.

The first stage of the process is the conversion of the complex organic wastes to organic acids. This process is completed by acid-forming bacteria. The second stage of the process is the conversion of the organic acids to CH_4 and CO_2. This second stage which stabilizes the waste is accomplished by methane-forming bacteria (McCarty, 1964; Merkel et al., 1969). For stable digestion of wastes to occur, a balance between the activities of the two bacteria groups must be established. Without sufficient methane-producing bacterial activity, sufficient quantities of organic acids will be produced to stop all CH_4 production. Eventually, all digestion ceases, and a sour tank of manure will result (Merkel et al., 1969). The process model provided by McCarty (1964) is shown in Figure 2.1.

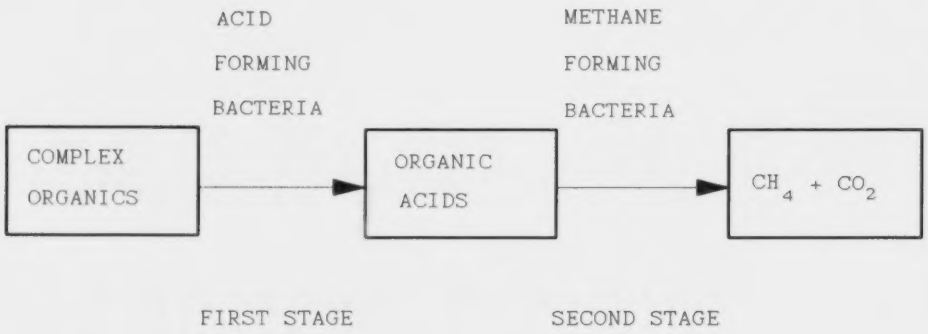


Figure 2.1 Two stage anaerobic digestion

(Adapted from McCarty, 1964)

The model of anaerobic decomposition provided by Barber and McQuitty (1974) is shown in Figure 2.2.

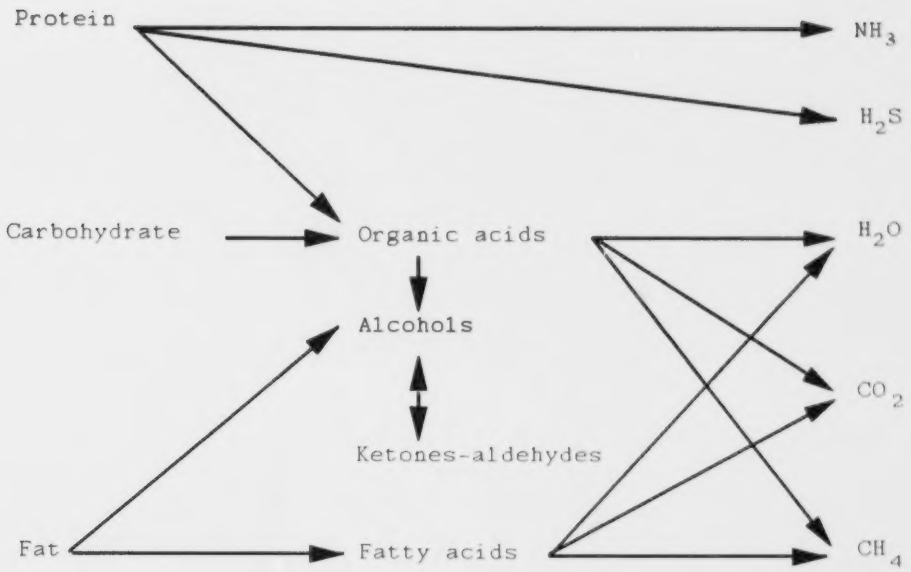


Figure 2.2 Anaerobic degradation of manure organics.

(Adapted from Barber and McQuitty, 1974)

The organic fraction of manure consists of proteins, carbohydrates and fats. Anaerobic decomposition degrades the proteins to NH_3, H_2S and short chain organic acids. The carbohydrates degrade to organic acids which, together with the acids formed from proteins, are further converted to alcohols, H_2O, CO_2 and short chain hydrocarbons including CH_4. The fats decompose to fatty acids and alcohols, and the fatty acids in turn form H_2O, CO_2 and CH_4. The alcohols are subject to oxidation reactions resulting in the formation of aldehydes and ketones. Ammonia may react

with alcohols and organic acids resulting in mercaptans and thioacids. Reactions between sulphides and the short chain hydrocarbons also are possible and result in disulphide compounds.

2.2 Gases from anaerobically treated animal wastes

Manure undergoes anaerobic digestion resulting in the release of at least 40 different gases, many of which are toxic or irritating (Donham et al., 1977). Among these gases, H_2S, CH_4, NH_3 and CO_2 comprise by far the major part. The presence and occupational hazards of these gases has been fully documented (Noren, 1977; Donham et al., 1988; Groves and Ellwood, 1991). Large quantities of gas can accumulate in liquid manure during storage, and are rapidly released during agitation or pumping operations (Noren, 1977; Groves and Ellwood, 1991). Human and animal health problems associated with gases within livestock confinement buildings include irritation of the eyes, mucous membranes, and respiratory tract from H_2S and NH_3 (Donham et al., 1977; Donham and Gustafson, 1982) and acute toxic incidents (fatal and near fatal) from H_2S (Noren, 1977; Donham et al., 1982).

Donham et al. (1988) monitored the gas production rate of three liquid swine manure storage structures for over a 12-month period. The three storage structures were under the farrowing building, nursery unit and finish unit, respectively. Table 2.1 shows summer and winter gas production rates from these three storage facilities.

Table 2.1 Summer and winter gas production rates*

Pit	Farrowing		Nursery		Finishing	
	Summer 27 June-24 Sept.	Winter 24 Sept-20 Jan.	Summer 25 June-15 Sept.	Winter 26 Oct.-19 Feb.	Summer 11 July-24 Sept.	Winter 4 Nov.-March
Temperature (°C)						
Mean	23	13.1	25	17.7	22	9.3
Minimum	18	11.0	22.5	19.0	24	2.0
Maximum	28	15.5	29	19.0	24	13.0
Total gas production (m^3/1000 m^3/day)						
Mean	224	72.2	19.5	8.12	22.4	3.4
Minimum	141	35.5	6.8	5.24	10.6	1.8
Maximum	341	124.2	45.0	25.05	30.2	5.0
CH_4 gas production (m^3/1000 m^3/day)						
Mean	151	51.6	10.6	5.32	7.2	1.1
Minimum	93	27.7	3.6	3.38	2.9	0.5
Maximum	237	87.7	26.8	16.10	10.52	2.5
CO_2 gas production (m^3/1000 m^3/day)						
Mean	73	20.7	8.8	2.77	15.2	2.28
Minimum	46	7.5	3.1	1.86	7.7	1.38
Maximum	104	38.0	18.2	8.92	20.6	3.40
H_2S gas production (m^3/1000 m^3/day)						
Mean	22.0	8.35	3.3	0.326	11.9	0.90
Minimum	0.6	0.75	0.8	0.055	6.5	0.02
Maximum	31.6	20.2	5.4	2.482	17.4	1.80

* Adapted from Donham et al., 1988

Donham et al. (1988) noted that, in general, gas production from the farrowing storage pits was 8 to 20 times higher than gas production from pits in the other two facilities. This was due to the high NH_3 and volatile acid content in the

latter two storage structures that appeared to inhibit biological activity. When manure temperatures dropped below 18°C, there was a significant decrease in gas production. Therefore gas production was significantly less in the winter than in the summer.

Table 2.2 Content of gas evolved from swine manure*

Pit	Farrowing	Nursery	Finishing
CH_4 content (%)			
Mean	70.9	56.1	36.6
Minimum	65.2	30.1	15.6
Maximum	78.8	71.4	65.8
CO_2 content (%)			
Mean	29.1	43.9	63.4
Minimum	21.2	28.6	34.2
Maximum	34.8	70.0	84.4
H_2S content (ppm)			
Mean	1320	1380	10900
Minimum	43	116	96
Maximum	5690	6040	75900

* Adapted from Donham et al., 1988

The composition of manure gases evolved from the three storage structures is shown in Table 2.2. The concentration of H_2S of gases evolved from farrowing and nursing storage structures were comparable, but much lower than the finishing storage pit. The water supply for these buildings contained low sulphate

concentrations. Therefore, organic sulphur was the main precursor for H_2S. The mean concentration of H_2S for farrowing and nursing were 1320 ppm and 1380 ppm with a maximum value of 5690 and 6040 ppm, respectively. The mean concentration of H_2S trapped over the liquid of a finishing pit was 10900 ppm with a maximum value of 75900 ppm. This peak value occurred after cleanout between 2 and 12 May. Prior to cleanout the mean concentration of H_2S of manure gas was 4020 ppm with a maximum value of 16500 ppm. Following cleanout to 16 June, the mean concentration of H_2S was 67700 ppm, with a maximum value of 75900 ppm.

Donham et al. (1988) concluded that, in general, the H_2S content of gases evolved from liquid manure showed much more variation than CH_4 or CO_2 content. To prevent H_2S poisonings, one must be especially cautious of the high H_2S production and hazard during warm months. For at least 50% of the cases, maximum recommended ventilation rates may not be sufficient to prevent acute toxicity during manure agitation.

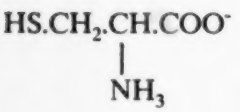
Groves and Ellwood (1991) investigated gas evolution during the handling of animal slurry at five sites (Four of them were cow units and one of them was a pig unit). They concluded that the main toxic gas hazard was H_2S, which presented an acute rather than a chronic risk. High concentrations (up to 141 ppm) were found in slurry pits. Even higher transient concentrations (up to 541 ppm) were found. The period of greatest risk was at the start of mixing. Even in open well-ventilated barns there is a danger of high transient H_2S levels.

2.3 Sources of H_2S in anaerobic animal wastes

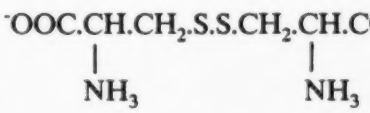
Barber and McQuitty (1974) noted that the two most important sources of sulphides (or H_2S) in anaerobic manure storages are dissimilatory sulphate reduction, and anaerobic protein degradation. The reduction of sulphate, and other inorganic oxidized forms of sulphur, to sulphide is accomplished by plants and a wide variety of microorganisms. Plants and many bacteria are capable of assimilatory sulphite reduction which is the reduction of sulphate to sufficient sulphide to meet the nutritional requirements of the organism. A few microorganisms, including a variety of yeasts and a small group of anaerobic bacteria, are capable of dissimilatory sulphate reduction with the production of massive quantities of sulphide. In dissimilatory sulphate reduction, the organisms use sulphate as the terminal electron acceptor in their energy metabolism.

Hydrogen sulphide may be produced under anaerobic conditions even in the absence of sulphate reducing bacteria. Both chemical and enzyme-facilitated bacteria transformations have been implicated. Sulphur-containing amino acids, cysteine/cystine and methionine can be degraded enzymatically to organic acids, NH_3, amines, H_2S and mercaptans by heterotrophic bacteria in a process commonly termed as putrefaction.

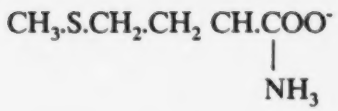
The molecular formula of sulphur-containing amino acids is as follows:



Cysteine



Cystine



Methionine

2.4 Properties of H_2S in anaerobic animal wastes

Hydrogen sulphide is a colourless gas having the characteristic odour of rotten eggs. It is slightly denser than air. And it is inflammable, burning in air with a pale blue flame. The typical "rotten-egg" odour of H_2S is detectable by the olfactory at very low concentrations (0.025 ppm) in the air. At concentrations of 200 ppm, H_2S is distinctly dangerous. When concentrations reach 500-1000 ppm, it will produce manifestations of acute intoxication after a few minutes of exposure (NRC, 1979). The Short Term Exposure Limit (STEL) is 15 ppm (ACGIH, 1982).

Soluble sulphides exist in anaerobic manure as dissolved hydrogen sulphide ($H_2S_{(aq)}$), bisulphide ions (HS^-) and S^{2-}. These three forms are collectively termed total soluble sulphides.

In the slurry, $H_2S_{(aq)}$ is partially ionized to H^+ and HS^-.

$$H_2S_{(aq)} \rightleftharpoons H^+ + HS^-$$

Further ionization of HS^- yields S^{2-} and additional H^+.

$$HS^- \rightleftharpoons H^+ + S^{2-}$$

The tendencies for $H_2S_{(aq)}$ and HS^- to dissociate are governed by their dissociation constants.

Desorption of $H_2S_{(aq)}$ results in an accumulation of gaseous hydrogen sulphide ($H_2S_{(g)}$). The concentration of $H_2S_{(g)}$ is directly proportional to the concentration of $H_2S_{(aq)}$. Two other important factors which influence the concentration of $H_2S_{(g)}$ released from manure are pH and temperature.

2.5 Control of H_2S from anaerobic animal wastes

Barber and McQuitty (1974) suggested three general ways to reduce the concentration of H_2S in the atmosphere surrounding anaerobically digested animal manure. The three ways are:

1) minimize the concentration of $H_2S_{(aq)}$;

2) minimize the desorption of $H_2S_{(aq)}$;

3) minimize the dispersion of $H_2S_{(g)}$.

The details of each of these three ways to reduce the concentration of H_2S are summarized in Figure 2.3.

2.6 Oligolysis treatment of pig manure

The oligolysis treatment process attempts to minimize the concentration of $H_2S_{(aq)}$ by the dissociation of $H_2S_{(aq)}$ and the formation of iron precipitates.

Oligolysis is an electro-chemical treatment process. Two electrodes are immersed in slurry and a voltage is applied across the electrodes. The electric potential causes ferrous ions (Fe^{2+}) to be released by the anode into the slurry. These Fe^{2+} combine with S^{2-} ions that are available in the slurry forming ferrous

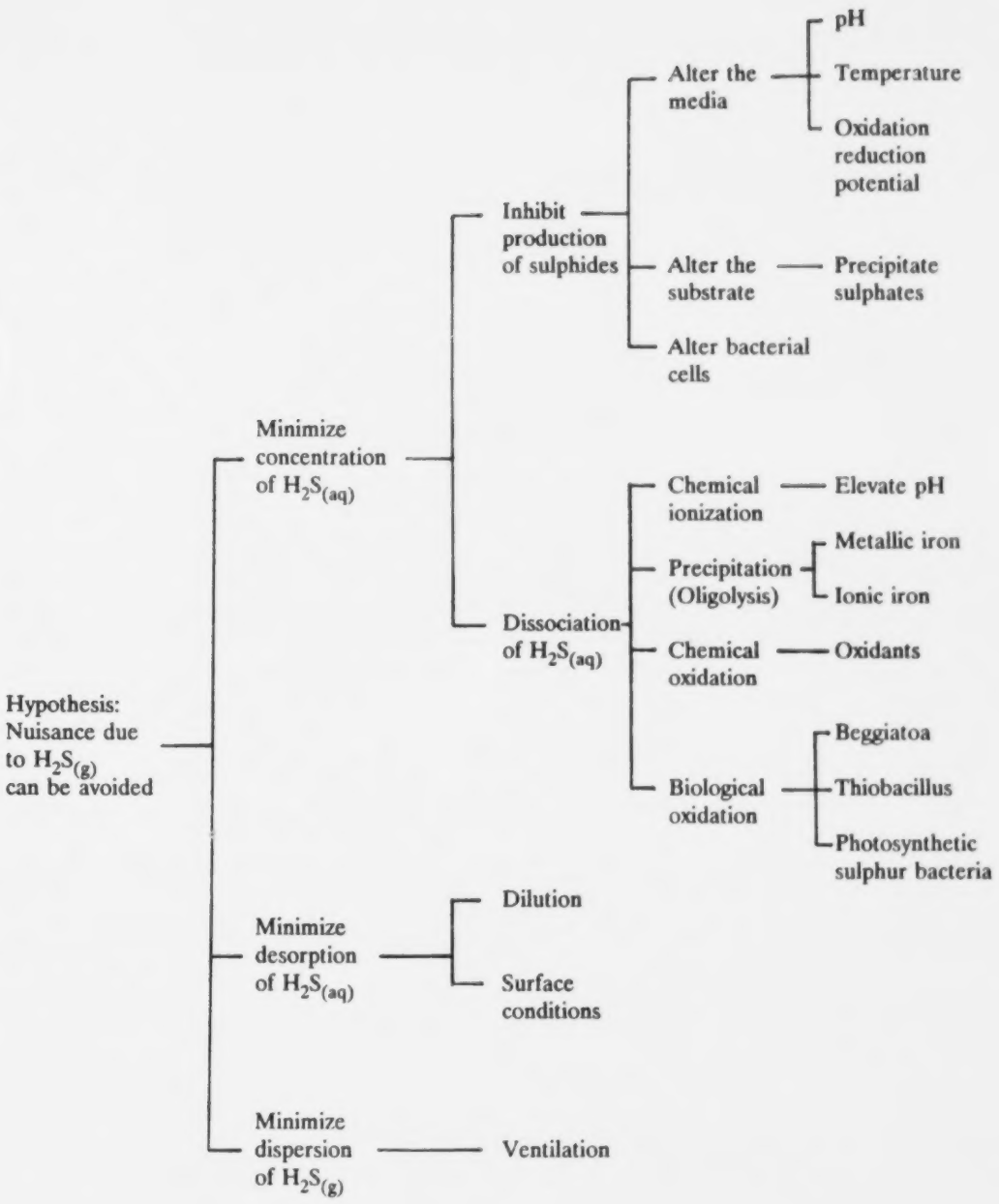


Figure 2.3 Control of H_2S from anaerobic manure

(Adapted from Barber and McQuitty, 1974)

sulphide (FeS) precipitate which is insoluble. If these S^{2-} ions were not captured by the Fe^{2+} ions then other sulphur compounds would be formed in the slurry, for example H_2S. The chemical reactions that take place in an anaerobic medium are those summarized in Figure 2.4 (Yu et al., 1991).

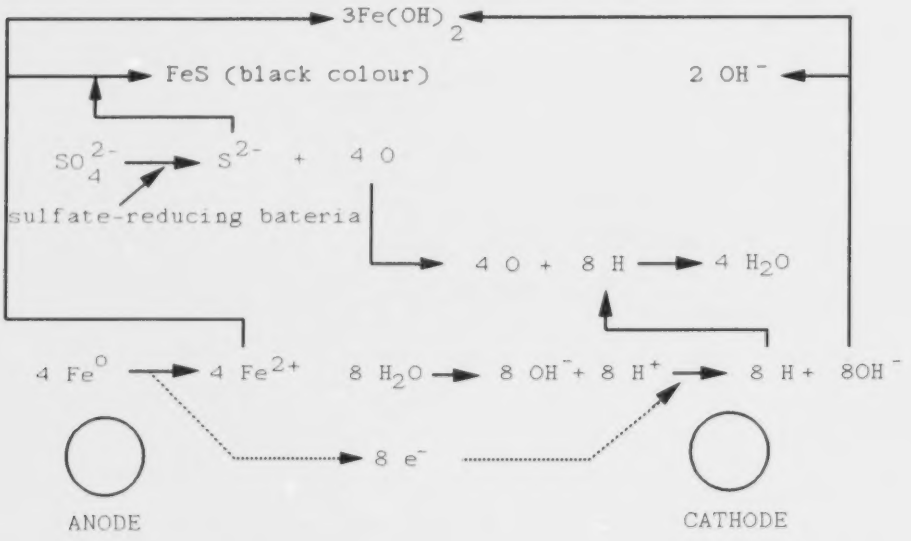


Figure 2.4 A graphical presentation of the oligolysis treatment

(Adapted from Yu et al., 1991)

Chiumenti et al. (1987) compared the treatment of swine manure by aeration with oligolysis. An aeration system was installed in a 2000 m^3 storage basin. The total installed power was 12 kW. An oligolysis treatment system was installed in a 1750 m^3 storage basin. The system consisted of a copper electrode and a coal

electrode. The distance between the electrodes was more than 45 m. The electric potential applied to the electrodes varied between 10 to 20 volts and the current was varied between 2 to 2.5 amps. The system was operated on a one hour cycle such that during the first 45 minutes cupric ions were produced, then for the following 15 minutes the current was reversed and partial reabsorption was achieved. About a week prior to land application, a third metallic electrode was used to reabsorb the cupric ions. The test was conducted for 120 days. During spreading of the slurry, it was found that both treatments provided significant odour reduction. A comparison of the energy requirements of the two systems indicated that the aeration system required 15-20 W-hr/head per day while the oligolysis system required 1.7-2.2 W-hr/head per day.

In another experiment (Chiumenti and Donantoni, 1988), 10 to 20 volts was applied between a copper and a coal electrode, with a current of 0.8 to 1.0 A. The unit operated on a 60-min cycle. Copper ion production occurred in the first 45 minutes with partial resorption occurring in the following 15 minutes by reversing the electrolytic flow. About one week before the spreading of the slurries, the exchange process was reversed with resorption of copper ions in order to reduce their final concentrations in the slurry. This experiment was carried out on a commercial scale piggery, where 1500-2000 pigs were fattened per year. The piggery had a totally slotted floor with an underlying slurry collection and storage tank. The two electrodes were positioned on the walls of this tank which was 3 m deep and had a capacity of 1750 m^3. The experiment lasted 120 days. The results showed that the

oligolysis treatment can reduce concentration of offensive piggery gases, decrease the diffusion radius of odours in the case of forced ventilation, and completely remove the offensive odour during spreading. The energy required for the oligolytic treatment was much less than that necessary for the aerobic treatment.

Yu et al. (1991) compared the odour from pig manure treated by oligolysis and two proprietary odour reducing agents; Bio-gest and Nature-aid in term of thirteen odour causing compounds. Feces, urine and water spillage were collected every second day from below the dunging area of three pens of six pigs. The manure was stored in 12 bioreactors. Three of them, which were subject to oligolysis treatment, had two iron bars inserted in the barrels. The three bioreactors were electrically connected in series. An electrical potential of 12 volts was applied to these bioreactors. The treatment time was 8 weeks.

Yu et al. (1991) concluded that the oligolysis treatment yielded no statistical differences from the control treatment with the exception of propionic acid being lower in the oligolysis treatment in the liquid phase. They also concluded that the oligolysis treatment removed 95% of the H_2S in the gas phase of the treated pig manure and reduced the odour nuisance of the treated pig manure. These observations indicated that oligolysis is effective in reducing the H_2S evolution from anaerobic digestion but that oligolysis does not interrupt the anaerobic digestion process. And oligolysis will probably control nuisance odour since odour appears to be due to the presence of H_2S and other sulphur-containing compounds.

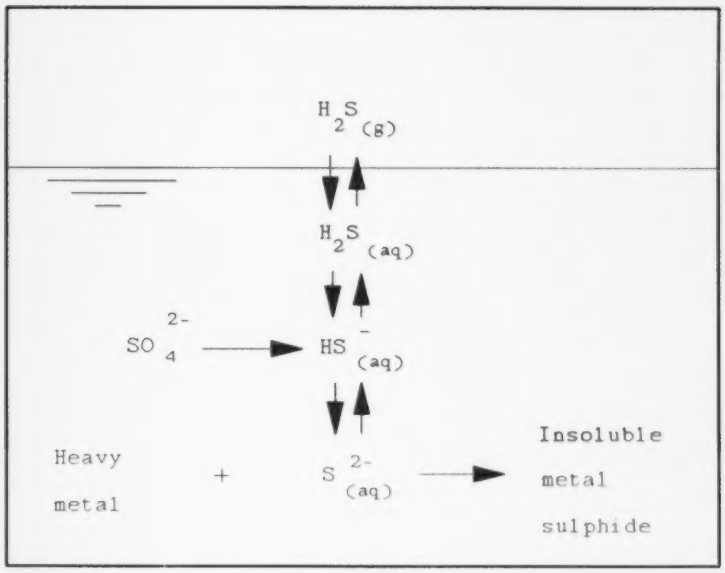


Figure 2.5 Schematic of the interaction between heavy metals and $H_2S_{(g)}$ in an anaerobic digester.

(Adapted from Lawrence and McCarty, 1965)

Lawrence and McCarty (1965) derived a technique for detecting the presence of potentially harmful concentrations of toxic metals in sludge fed to anaerobic digestion units in waste treatment plants. The series of redox, heterogeneous, and acid-base equilibria are shown in Figure 2.5. With a normal level of metals in the digester, the $H_2S_{(g)}$ value will be constant and can be measured. If a high concentration of heavy metals is fed to the digester, more metal sulphide solids will form and the concentrations of S^{2-}, HS^- and $H_2S_{(aq)}$ will decrease. These will be accompanied by a fall in $H_2S_{(g)}$, since its concentration is determined by $H_2S_{(aq)}$. By

determining the acceptable range of H_2S levels in the digester, an early warning system for toxic levels of heavy metals is available. The mechanism of this technique is similar to oligolysis treatment of manure, except that in oligolysis treatment, the metal ions are introduced to the slurry from anode by the voltage potential across the electrodes. This supports the concept of oligolysis.

2.7 Odour measurement

The odour from animal wastes are primarily caused by gases and organic compounds produced by the decomposition of organic matter in the storage of manure. About 80 compounds have been identified as products of degradation of anaerobic decomposition of livestock and poultry manure (Groves and Ellwood, 1991). Organics such as aliphatic amines, mercaptans, sulphides, organic acids and skatole are the major components of odour of animal manure (Burnett and Dondero, 1970; Merkel et al., 1969; Miner and Hazen, 1969).

Four independent factors have been suggested to completely characterize an odour: intensity, character, hedonics, and detestability. " To date, detestability is the only factor that has been used in the development of statutory regulations for nuisance odours "(Tchobanoglous and Burton, 1991).

The sensory (organoleptic), wet chemistry and gas chromatographic detection methods have been used to detect and measure odours. Both wet chemical and gas chromatographic methods are used to separate, identify, and quantify odour compounds.

The human nose offers up to 1000 times the sensitivity of other analytical procedures on certain odorous compounds (Elliott et al., 1978). It has been shown that, under carefully controlled conditions, the human sensory (organoleptic) measurement of odour by the olfactory system can provide meaningful and reliable information. However it suffers from a lack of specificity for individual odorants. Its primary advantage is qualitative capacity. Other limitations which affect the capacity of the human nose to effectively measure odour are adaption, fatigue, odorant concentration, temperature, illness, chemical reaction, age, sex, smoking habits, pungency, and uncertainty (Barth, 1973).

Wet chemical odour measurement lacks sensitivity and specificity. Odorants associated with animal production exist at low levels and concentrating procedures are often needed. Also odours can be masked by other aerial contaminants.

In contrast, gas-chromatography (GC) can be used to detect much lower ambient concentrations of odour compounds. GC is presently the most dependable procedure for identifying odorous manure components, but it cannot characterize the quality of the odour. To this end the procedure is often coupled with olfactory evaluation.

All methods of odour detection and measurement have limitations. None are simultaneously rapid, simple, inexpensive, and reproducible (Elliott et al., 1978).

The determination of odour emissions from animal wastes can only be done by means of odour panels. This is because no significant relationships have been found between the odorants in manure that can be measured objectively and the

intensity of the odour. This is probably because the odour of manure usually consists of a mixture of many odorants. Knowing the composition of manure odour along with the concentration of individual components does not explain the composite odour, qualitatively, or quantitatively. Combination of only two of the principal odour components, in varying concentrations, elicited all of the five possible results of the combination-addition, reduction, independence, synergism, and averaging. Controlling one odorant emitted in the waste treatment process can provide significant odour reduction by limiting the odorant interactions by addition or synergism. Controlling one odorant would be easier than controlling all or most of the significant odorants present (Hill and Barth, 1976).

Dilution is a basic technique that have been used for sensory odour measurement, because it can greatly aid the precision of such tests (Barth and Melvin, 1984). Both liquid and vapour dilution techniques are useful depending on the state of the material to be tested. Liquid dilution procedures are conducted under controlled conditions, but vapour dilution techniques are adapted to field and laboratory situations.

The T.O.N. is the greatest dilution of sample with odour free water yielding a definitely perceptible odour. The amount of dilution required is related to odour level. The recommended sample size is 200 mL. This method is applicable to samples ranging from nearly odourless natural waters to industrial wastes with threshold numbers in the thousands. There is no absolute threshold odour concentration, because of inherent variation in individual olfactory capability.

The numerical value of the T.O.N. is determined as follows:

$$\text{T.O.N.} = \frac{A+B}{A}$$

where: A= mL of sample and B= mL of odour free water.

The odour emanating from the liquid sample is determined with human subjects (often a panel of people). For most purposes, the T.O.N. of a odour panel is expressed as the geometric mean of individual T.O.N.

3. PRELIMINARY TEST

Preliminary tests were carried out at the University of Alberta to test the effect of current on H_2S removal. In the experiment, three different levels of DC current were applied with one control, with each level applied to 3 bioreactors. The current levels used were 0.15, 0.25 and 0.35 A. All bioreactors were treated for a 3-week period. The current levels were controlled through the use of constant current power supplies. The voltages across the electrodes of the bioreactors were allowed to fluctuate freely and were measured daily.

The voltage across the bioreactors treated with 0.15 and 0.25 A increased continually over time. By day 7, the average voltage levels were 1.3 and 2.1 volts, respectively. While the applied voltage levels across the bioreactors treated at 0.35 A followed this same pattern initially, by day 7, the mean voltage level was 3.3 volts, then it began to fluctuate erratically.

Gas samples were obtained weekly by connecting a 500 mL gas sampling bulb to an opening located at the top of each bioreactor. The gas sampling bulbs were connected to the bioreactors for a minimum of 48 h and then removed for measurement of H_2S using a Sulphur Chemiluminescence Detector (SCD) mounted on a GC.

The results of the gas analysis are summarized in Table 3.1. A significant reduction in the H_2S concentration occurred in the gas generated from the treated

bioreactors. There appeared to be a strong correlation between voltage and current levels and reduction in H_2S concentration. The barrels treated at 0.35 and 0.25 A had much lower H_2S concentrations than the barrel treated at 0.15 A. The higher voltage required to generate the constant current appeared to be responsible for the higher efficiency of removal. After two weeks of treatment with 0.25 and 0.35 A, the H_2S concentration of the gas released from bioreactor was reduced to 5 and 6.5 ppm, respectively.

Table 3.1 Concentration of H_2S of treated pig manure (mg/L)

Treatment	1 week	2 weeks	3 weeks
Control	3981	7641	3144
0.15 A	7216	4193	1246
0.25 A	2225	5	0.1
0.35 A	360	6.5	0

From these results, it was concluded that applied voltage levels may be an important factor in optimization of the process. Voltages of 2 to 3 volts appeared to be optimum for the 0.225 m^3 capacity bioreactor.

The voltage level across the electrodes is dependent on the thermal potential required for the oxidation of iron (approximately 0.44 volts), electrical conductivity of the slurry, the electrode area, spacing and the amount of crusting occurring around the electrode. If the voltage level is higher than necessary chemical reactions other than those desired will occur. On the other hand, high voltage level will increase the energy costs and iron consumption. If the voltage level is lower than necessary, not

enough Fe^{2+} will be dissolved and the effectiveness of the oligolysis process will be reduced (Feddes, 1991). From the economic point of view, the voltage level must keep as low as possible in order to reduce the cost.

4. OBJECTIVES

The objective of this study was to determine whether voltage influences the effectiveness of the oligolysis process in removing sulphide and odour by:

1. chemical analysis, and
2. T.O.N. measurement.

5. EXPERIMENT

The oligolysis treatment experiment was conducted at the Edmonton Research Station (University of Alberta, Edmonton, Alberta). The research commenced on Nov. 2, 1992 and ended on March 30 of 1993.

5.1 Experimental Apparatus

The equipment used to treat the manure with oligolysis consisted of the following:

1) 12 - 0.225 m^3 capacity plastic barrels

2) Model 5985-80 Digi-sense pH meter

3) Fluke 8022B Digital Multimeter

4) Hydroma SP50 A1 manure pump

5) Tedlar 232-08 (10 L) sample bags

6) 19 mm mild steel rods 914 mm in length

7) Voltage regulators

8) 50 mL disposable plastic syringes

9) Screw cap test tubes with hungate caps and septa

10) Tygon tubing

11) Plastic nalgene sampling bottles

12) Mettler P2010 weigh scale

13) Power supply

14) Dow Corning 732 multi-purpose sealant.

The experimental apparatus used to carry out the T.O.N. test were as follows:

1) 500 mL glass erlenmeyer flasks

2) 20 mL, 10 mL, 5 mL Pipets

3) 200 mL measuring flasks

4) Constant temperature waterbath (60°C)

5) Odour free water

6) Aluminum foil

7) Thermometer.

5.2 Experimental Design

The experiment was arranged according to a randomized complete block design with time split. Six treatments (5 voltage levels and control) were used, with each treatment applied to two bioreactors. From the preliminary test, 2 to 3 volts appeared to be optimal. The five voltages selected in this experiment were 1.5, 2, 2.5, 3, 3.5 volts. Voltages were held constant by voltage regulators. Each trial occurred over a 15-day period. The first 8 days were for establishing a reference point and the following 7 days were for treatment. The whole experiment was repeated four times (4 blocks).

An experiment carried out by Coleman et al. (1992) at the Alberta

Environmental Centre indicated that the oligolysis is a rapid process. In their experiment, 2 L bioreactors were used. Liquid samples were taken at 15, 30 and 60 minutes intervals for the measurement of free sulphide and total sulphide. Gas was sampled for H_2S by continuously purging the bioreactor head space with nitrogen and passing the effluent bioreactor gas through a zinc acetate H_2S trap. The conclusions were that the free sulphide is effectively and rapidly bound as an insoluble form reducing the H_2S emission to air. The oligolysis reaction was rapid with approximately 85% of free sulphide being removed within the first 1.5 h.

Based on the above observations, liquid samples were obtained during the first day at 0, 0.5, 3, 24 h and on day seven (168 h), while gas samples were obtained at 0, 24 and 168 h after treatment was initiated.

5.3 Experimental Procedures

5.3.1 Experiment set up

Pigs were housed in a growing-finishing building with a total floor area of approximately 30 x 10 m. Two slatted slurry channels, each 1.4 m wide and 0.7 m deep, ran the length of the building at the rear of the pens. These two channels were routed to a collection pit at the end of the building. The plan view of the building is shown in Figure 5.1.

The slurry in the pit consisted of animal manure, drinker spillage and waste feed. Since pig slurry settles into two layers: a dense sludge at the bottom and a thin watery effluent on top (Ellwood and Groves, 1991), prolonged mixing of the settled

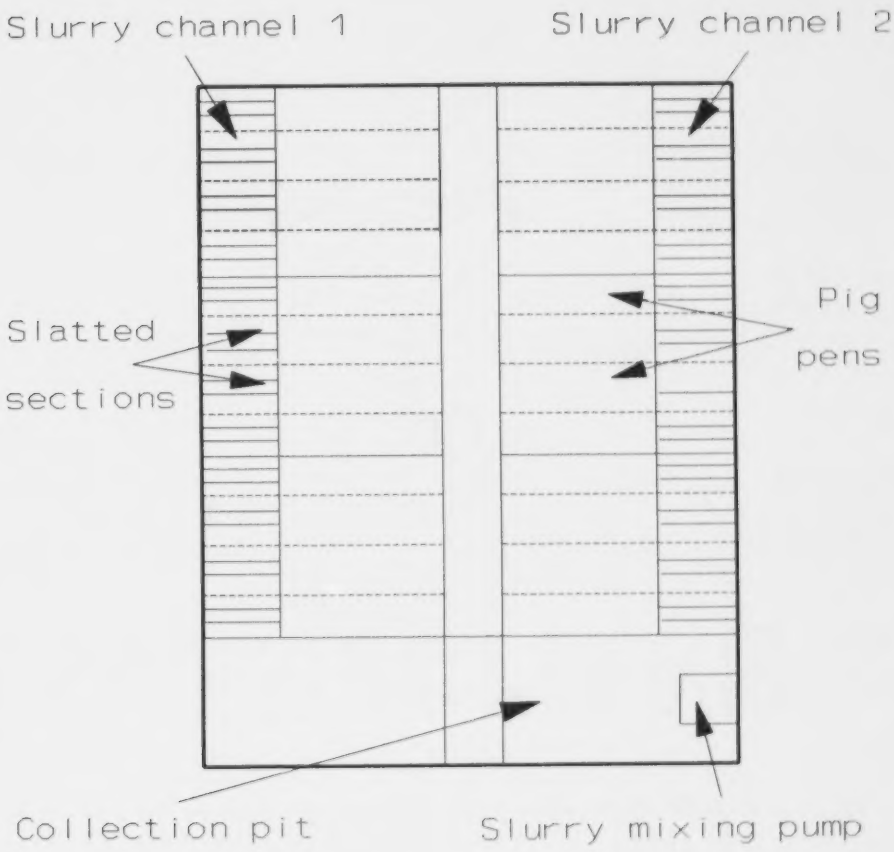


Figure 5.1 Plan view of piggery

slurry was required before the material was pumped into the barrels.

Ten plastic barrels treated with oligolysis were set up as shown in Figure 5.2. Tubing to obtain samples of liquid and gas were mounted in the top of the barrel. The liquid sample tubing was inserted 120 mm below the liquid level. Gases generated from the pig manure in the barrels were collected in Tedlar sample bags. The iron bars projected 838 mm into the barrel with the remaining bar projecting outside the barrel. The distance between two iron bars was 315 mm. Two remaining barrels which served as controls were similar to the treated barrels except without iron bars. The barrels were filled to 94% capacity. All the bioreactors were located in a small, ventilated, temperature-controlled room within the barn. The room temperature was maintained at 20°C.

5.3.2 Experimental procedures

The experimental procedure used to start up the experiment was carried out as follows:

1) Mix contents of pit for 30 minutes to achieve complete mixing.

2) Fill the barrels in randomized order.

3) Seal the barrels with sealant to prevent any leakage.

4) Connect gas bag to each barrel.

5) After 8 days, sample the contents.

6) Weigh iron bars, put into bioreactors and begin treatment.

7) Monitor voltage and current levels regularly.

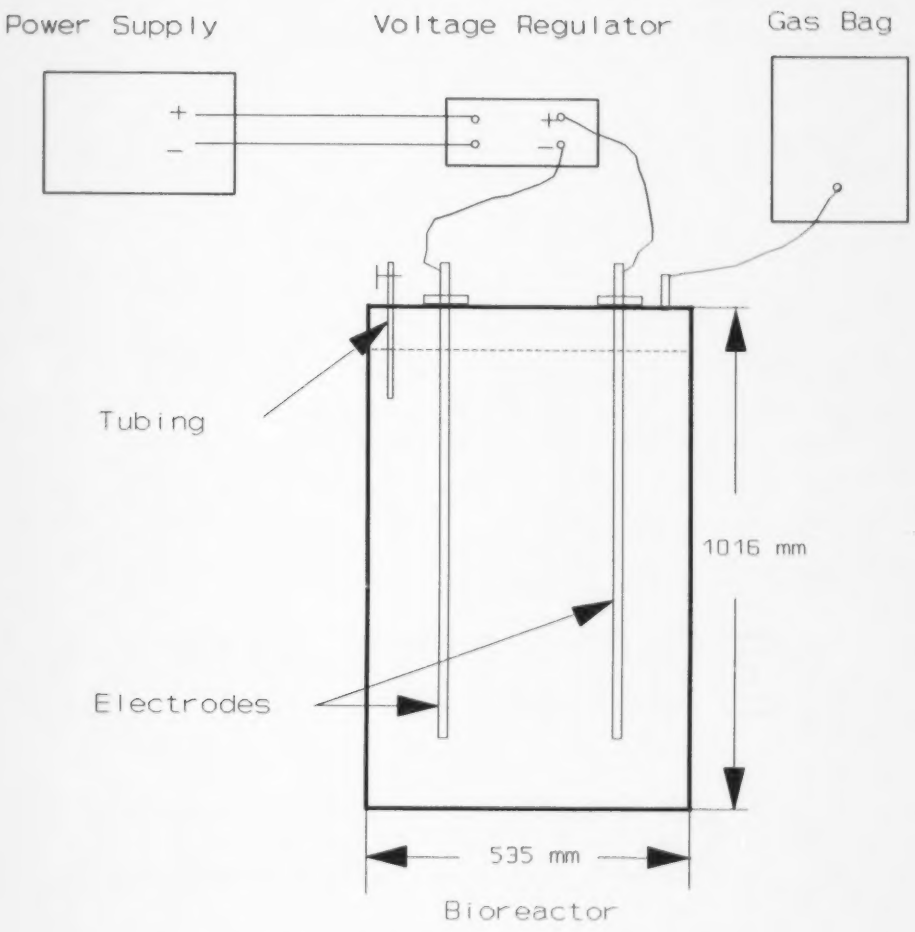


Figure 5.2 Bioreactor used in the experiment

8) Take gas and liquid samples according to schedule.

9) Measure pH level whenever sampling occurred.

10) Weigh iron bars after treatment.

5.4 Sampling

Liquid samples were obtained by a syringe and then transferred to a Hungate tube, filled to within 5 mm from the stopper, capped and frozen for shipment to the Alberta Environmental Centre for analysis. To minimize oxidation, samples were stored under nitrogen at 4°C until analysis at Alberta Environmental Centre.

Gas samples were collected using Tedlar bags, the valves were closed tightly before removal from the barrels. The gas samples were kept at room temperature then shipped to Alberta Environmental Centre for analysis.

5.5 Analyses

The free sulphide in anaerobic treated manure is defined as the collection of $H_2S_{(aq)}$, HS^- and S^{2-} (George, 1993). An equation relating the concentration each is given as follows:

$$[\text{Free sulphide}] = [H_2S_{(aq)}] + [HS^-] + [S^{2-}]$$

In the slurry, equilibrium equations exist as follows:

$$H_2S_{(g)} \rightleftharpoons H_2S_{(aq)}$$

$$H_2S_{(aq)} \rightleftharpoons H^+ + HS^-$$

$$HS^- \rightleftharpoons H^+ + S^{2-}$$

The concentration of $H_2S_{(g)}$ is proportional to the concentration of free sulphide, if the concentration of free sulphide can be kept to a minimum, the amount of $H_2S_{(g)}$ released from manure also would be minimized. The liquid samples were analyzed for free and total sulphide. The gas samples were analyzed for H_2S. The analysis methods are as follows:

Total sulphide: The gas dialysis/methylene blue method was employed using 6N HCl to release the gas (hydrogen sulphide) before separation from the sample by a gas dialysis membrane, followed by colour formation and detection. This procedure allows for zinc preservation and the use of ascorbic acid as an antioxidant. The method has been described in detail by Francom et al. (1989).

Free sulphide: A method was developed by Coleman et al. (1992) for pig waste slurry specifically for oligolysis study by modifying the total sulphide as follows: samples were stored in Hungate tubes with gas tight butyl rubber septa. Sub-samples were withdrawn from the Hungate tubes by syringe and diluted with distilled deionized water immediately prior to analysis. No HCl was used allowing the naturally occurring $H_2S_{(g)}$ to transfer across the gas dialysis membrane prior to colour formation and detection.

Hydrogen sulphide: The concentration of H_2S was determined by GC and SCD (Shimadzu GC-9A, Sievers 350). The operating conditions of the GC were as

follows:

Oven temp = 80°C

Injector detector = 44°C

Column: chromsil 330

N_2 = 20 mL/min (carrier gas)

H_2 = 139.5 mL/min

Air = 400 mL/min, and

Integration time = 0.03 seconds.

5.6 Gas production

Gas production was measured by placing a container filled with water inside a tray. The sample gas bag was placed in the container and pressed down until submerged. The volume of the water that overflowed from the container into the tray minus the volume of the gas bag represented the volume of gas.

5.7 T.O.N. measurement

In order to detect the effect of treatment on the removal of odour, the T.O.N. measurements were conducted on the 168 h liquid samples.

5.7.1 Odour panel

The measurement of T.O.N. was undertaken according to Standard Methods for the Examination of Water and Wastewater 16th edition, 1985. The odour panels

consisted of students and employees of the Department of Agricultural Engineering, University of Alberta. The size of each panel was five or more persons. No preliminary testing or selection of panelists was undertaken. However, after several runs were made some particularly insensitive persons were eliminated. The panelists did not eat or smoke prior to the test. The testing room was air conditioned and free of background odours. Each panel member made his evaluation independently. The sample temperature was 60°C.

5.7.2 Procedures of T.O.N. measurement

A preliminary test was undertaken before the real experiment was conducted. During the preliminary test, the range of the threshold odour was found to be between 1.4 to 2.0 mL of 1/1000 intermediate sample diluted to 200 mL with odour free water, i.e., dilutions of 7 ppm (parts per million) to 14 ppm. Because the dilution was sufficient high, no colour difference which might bias panelist decision was noticed between samples.

The experimental procedure was carried out as follows:

1) Prepare an intermediate dilution first by diluting 2 mL sample to 200 mL with odour free water. Then add 20 mL of this solution to a flask and dilute it to 200 mL again. This dilution of 1000 ppm was used as an intermediate sample.

2) Prepare flasks containing 0.5, 1.0, 1.4, 2.0, 2.8, 4.0, 5.7 mL intermediate sample and dilute each to 200 mL with odour free water. The concentrations of these

samples were 2.5 ppm, 5 ppm, 7 ppm, 10 ppm, 14 ppm, 20 ppm, 28.5 ppm of the original sample. Prepare three flasks containing 200 mL odour free water as blanks. All the samples were stored in 500 mL erlenmeyer flasks and covered with aluminum foil.

3) Preheat above samples to 60°C in a constant temperature water bath.

4) Present samples to panelists from the lowest concentration to the highest concentration.

5) Instruct panelists to shake flasks, remove covers, and sniff vapours.

6) Record observations by indicating whether odour is noted or not in each test flask.

7) Calculation. Calculate the T.O.N. of a panel as the geometric mean of T.O.N. of individual panelists.

6. RESULTS AND DISCUSSION

6.1 Liquid phase

The experimental free and total sulphide data for the liquid samples are listed in Appendix A. A total of 15 values are missing. Three of them were due to the breakage of sample tubes during transportation, while the others were the 0.5 h samples of the first run which were not analyzed due to laboratory problems encountered at the Alberta Environmental Centre. Also the liquid sample data of the third run were not included due to analysis problems.

Although the environmental factors were carefully controlled, it was not possible to obtain the same concentration of sulphide in each barrel after 8 days of fermentation. The free sulphide before the treatment ranged between 35.1 and 91.0 mg/L. The total sulphide before the treatment ranged between 40.7 to 128.1 mg/L. These values agreed with those reported by Donham et al. (1985). They found that total sulphide varied between 32.7 and 274.6 mg/L for pig manure. Therefore, the differences in the concentrations among different treatment levels may be due to the differences in the treatment levels and the differences in the initial concentrations. In order to see the treatment effect, the effect of initial concentration must be separated from the effect of the treatment. One way to do this is to use a ratio estimate, that is to present the concentration of free or total sulphide as the percentage of initial concentration. It also can be done by the

analysis of covariance by considering the initial concentration of free sulphide (FS) and total sulphide (TS) as covariates. Ratio estimate is the best when the following two conditions are satisfied:

1. The relation between concentration of sulphide (Y_i) and treatment (X_i) is a straight line through the origin.

2. The variance of Y_i about this line is proportional to X_i.

Although the relation between Y_i and X_i in this experiment was approximately linear these lines do not go through origin. This suggests an analysis based on the covariate rather than on the ratio estimate (Cochran, 1967). Analysis of covariance is a very versatile technique making it possible to control statistically variables that are not easily controlled experimentally. In this experiment it was assumed that:

1. There is no interaction between covariate and treatment, and

2. The regression of concentration on covariate after removal of block and treatment differences is linear and independent of treatment and blocks.

The two assumptions are valid for this experiment. The model equation for analysis of covariance is

$$\mathbf{Y_{ij} = u + TT_i + Bk_j + TT*BK_{ij} + bSO_{ij} + E_{ij}}$$

Where Y_{ij} is the ijth observation of concentration; u is the population mean; TT_i is the fixed effect of treatments; BK_j is the random effect of experimental blocks; $TT*BK_{ij}$ is the interaction effect of treatment i and block j; $S0_{ij}$ is the covariate (FS0 for free sulphide; TS0 for total sulphide); b is regression coefficient

of Y_{ij} on $S0_{ij}$; E_{ij} is the random experimental error.

The results of analysis of covariance of free and total sulphide are summarized in Table 6.1 and 6.2, respectively.

Table 6.1 Analysis of covariance (Free sulphide)

TIME (h)	TT	BK	TT*BK	FS0
0.5	=	***	=	=
3	**	***	=	=
24	***	***	=	=
168	***	=	*	=

*** significant at 0.001 level of probability
** significant at 0.01 level of probability
* significant at 0.05 level of probability
= not significant

Table 6.2 Analysis of covariance (Total sulphide)

TIME (h)	TT	BK	TT*BK	TS0
0.5	*	*	=	=
3	=	**	=	=
24	=	***	***	=
168	***	*	=	=

*** significant at 0.001 level of probability
** significant at 0.01 level of probability
* significant at 0.05 level of probability
= not significant

The first 0.5 h of treatment did not effect free sulphide levels. A treatment time of 0.5 h appeared to be too short to cause a difference in free sulphide level. However, in the sample times that followed, treatments all had significant effects.

Especially at time 24 h and 168 h, treatments were significant at $p<0.001$ level. For total sulphide, treatments were insignificant at time 3 h and 24 h. The treatment effect was significant at time 0.5 h and 168 h at levels of $p<0.05$ and $p<0.001$, respectively.

Blocks were all significant except at time 168 h for free sulphide. The major reason was likely due to the variation in manure composition since manure was pumped out at different times. This observation agrees with that made by Blouin et al. (1988). In their study, the composition of swine waste varied with different periods of the year on the same farm. Another reason appeared to be due to the difference of surface area of electrodes. The same electrodes were used in each barrel throughout the whole experiment which were cleaned and weighed after each run. Because of the mass loss of the electrodes, the surface areas of electrode were different among blocks. Since most of the free sulphide had been reduced to a very low level (close to zero) at 168 h, the block effects were insignificant for 168 h.

The least square means (LSM) of concentration of free sulphide and total sulphide is presented in Table 6.3 and 6.4, respectively. They are also shown graphically in Figure 6.1 and 6.2.

In addition to analysis of covariance, Fisher's LSD (least significant difference) procedure was employed to make a pairwise comparison among treatment means according to GLM procedure (SAS Inc. 1988).

Table 6.3 Concentrations of free sulphide (mg/L)[1]

Treatment	Time (h)			
	0.5	3	24	168
Control	74.0±9.0	78.7±6.2[a]	62.9±3.9[a]	43.3±1.8[a]
1.5 V	61.0±6.7	50.7±4.6[b]	34.6±2.9[b]	4.2±1.3[b]
2.0 V	67.5±8.3	57.3±5.7[ab]	30.4±3.6[bc]	2.7±1.7[bc]
2.5 V	62.1±6.3	57.0±4.3[b]	33.2±2.7[b]	0.5±1.3[bc]
3.0 V	62.7±7.2	54.4±4.9[b]	26.7±3.1[bc]	-0.1±1.5[c]
3.5 V	51.0±6.3	45.4±4.3[b]	21.4±2.7[c]	0.2±1.3[c]

[1] Least square means(LSM), and standard errors of LSM.
[a,b,c] Means in the same column with a different superscript differ at $p<0.05$.

Table 6.4 Concentrations of total sulphide (mg/L)[1]

Treatment	Time (h)			
	0.5	3	24	168
Control	91.1±8.8[a]	85.2±10.8	76.6±6.0	80.4±5.1[a]
1.5 V	54.9±5.4[b]	64.0±8.0	54.2±4.5	39.9±3.6[b]
2.0 V	47.5±7.4[b]	64.3±9.0	57.1±5.0	43.0±4.2[b]
2.5 V	61.5±6.5[b]	70.0±8.3	64.5±4.6	48.7±3.8[b]
3.0 V	58.9±7.1[b]	62.6±9.5	57.7±5.3	42.8±5.2[b]
3.5 V	58.1±5.3[b]	64.9±8.0	62.0±4.5	43.6±3.7[b]

1 Least square means(LSM), and standard errors of LSM.
[a,b,c] Means in the same column with a different superscript differ at $p<0.05$.

For free sulphide, at time 3 h, the control treatment had significantly higher concentration than voltage treatments except treatment level 2.0 V. At time 24 h and 168 h, the concentration of control treatment was significantly higher than all voltage treatments. Treatment level 3.5 V was significantly lower than treatment level 1.5 V and 2.5 V at 24 h. Treatment level 3.0 V and 3.5 V were significantly lower than treatment level 1.5 V at 168 h.

From Fig 6.1 and Table 6.3, it can be seen that the concentration of free sulphide for all voltage treatments decreased consistently with time. The mean concentrations of free sulphide for voltage treatments at 0.5, 3, 24 and 168 h were 60.8, 53.0, 29.3 and 1.5 mg/L, respectively. Over 52% of free sulphide had been removed in the first 24 h. From 24 to 168 h, an average of 6.7% of free sulphide had been removed each 24 h. This is because the electrodes were clean at the beginning of treatment. As the treatment progressed, FeS deposited on the cathode. The resistance between the electrodes was increased and the current level was reduced. Therefore, the efficiency of voltage treatment was reduced.

For concentration of total sulphide, at time 0.5 and 168 h, the control treatment was significantly higher than for all voltage treatment levels. No significant difference was observed among the different voltage levels. From Tables 6.3 and 6.4, it was observed that the total sulphide concentrations at 0.5 h under treatment levels of 1.5, 2.0, 2.5 and 3.0 V were lower than those of the corresponding free sulphide. The reason for this may be due to experimental error. The release of hydrogen

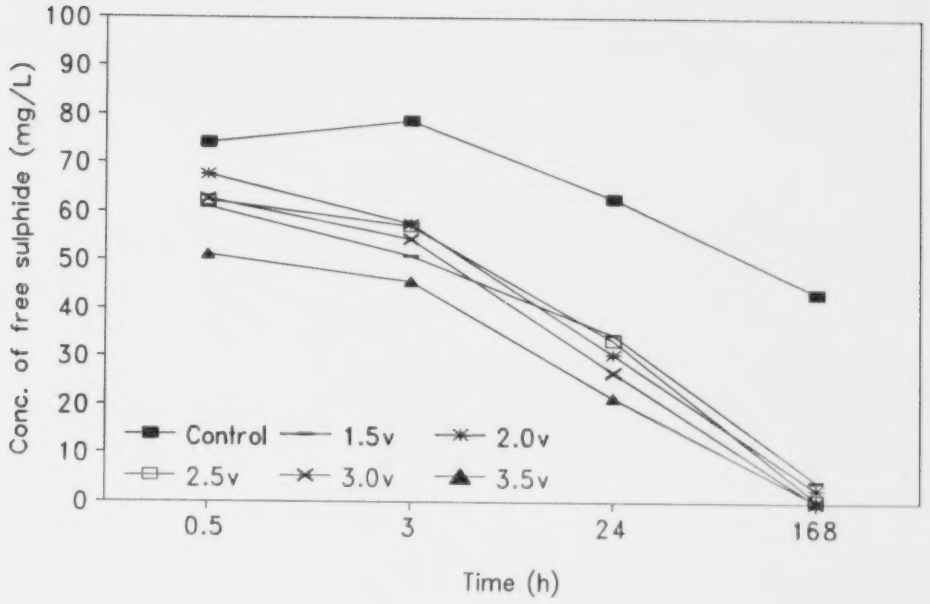


Figure 6.1 Concentrations of free sulphide (LSM)

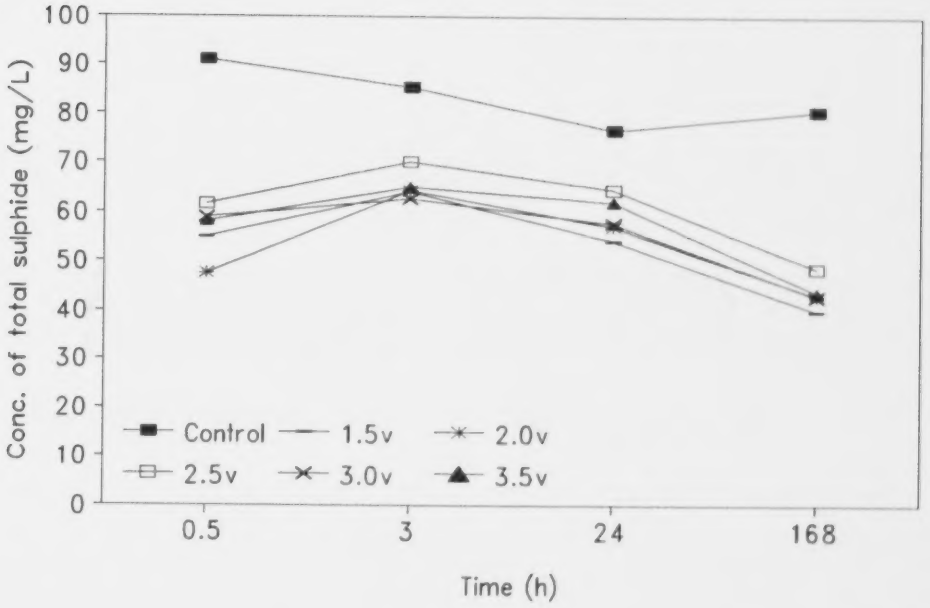


Figure 6.2 Concentrations of total sulphide (LSM)

sulphide during the chemical analysis may cause the decrease of total sulphide.

The mean concentrations of total sulphide in the voltage treatment of 0.5, 3, 24 and 168 h were 56.2, 65.2, 59.1 and 43.6 mg/L, respectively. As mentioned earlier, the concentrations of total sulphide for 0.5 h may have been erroneous. The mean concentration of total sulphide at 0.5 h was calculated in another way by assuming that 80% of the total sulphide were free sulphide at 0.5 h. Because the mean concentration of free sulphide at 0.5 h was 60.8 mg/L, so the corresponding total sulphide was 76 mg/L. Therefore the concentration of total sulphide also decreased with time. This is in contrast to the observation made by researchers at the Alberta Environmental Centre (Coleman et al., 1992). They indicated that the total sulphide remained constant during the treatment process. This may have been due to the mixing of their small bioreactor, thus resulting a homogeneous mixture. In this experiment, FeS deposited on the cathode and settled on the bottom of the bioreactors. No mixing occurred before sampling, thus there may have been less FeS in the supernatant where liquid samples were withdrawn. Therefore, the total sulphide may have decreased with the removal of free sulphide. Another reason was considered as the effect of the release of $H_2S_{(g)}$. In Coleman et al's (1992) experiment, treatment times were 6 hours, it was likely less $H_2S_{(g)}$ released compared with this experiment with treatment times of 168 h.

The mean concentrations of free and total sulphide at 0 h and 168 h are presented in Table 6.5. The percentage of free sulphide in total sulphide and the of 168 h concentration at a percentage of the 0 h concentration are also included.

Table 6.5 Mean concentrations of sulphide (mg/L)

	Free sulphide		Total sulphide		(%[1])	
	0 h	168 h (%[2])	0 h	168 h (%[2])	0 h	168 h
Control	72.8	45.8 (63)	88.9	76.7 (86.3)	(81.9)	(60)
Treated	53.7	1.04 (1.9)	65.8	45 (68.4)	(81.6)	(2.3)
Overall	56.7		70.9		80.0	

[1]. Percentage of free sulphide in total sulphide.
[2]. 168 h concentration as percentage of 0 h's concentration.

Table 6.5 shows that the mean free sulphide concentration of voltage treatments at 0 h was 53.7 mg/L. After the treatment, the mean concentration of free sulphide was 1.04 mg/L. More than 98% of free sulphide had been removed during the treatment process. The decrease of free sulphide in the voltage treatment was considered to be due mainly to the formation of FeS, which is inodorous. The FeS formed was not easily be separated and therefore prevented the participation of S^{2-} to other reaction. Another possibility was due to the release of hydrogen sulphide, but as the S^{2-} ions was used up by forming FeS, to re-establish an equilibrium between $H_2S_{(g)}$, $H_2S_{(aq)}$, HS^- and S^{2-}, less $H_2S_{(g)}$ would formed. This was confirmed by the analysis of gas samples, the concentrations of $H_2S_{(g)}$ released from the voltage treatment bioreactors were significantly lower than the control treatment.

The mean concentration of free sulphide in the control treatment was 72.8 mg/L at time 0 h and was 45.8 mg/L after treatment, which is 63% of initial concentration. This decrease may have been mainly due to the release of $H_2S_{(g)}$

which was very odorous. If the decrease of free sulphide was due only to the release of $H_2S_{(g)}$, the total sulphide would decrease with similar amount. But the results were that the free sulphide of control treatment decreased 30.8 mg/L (LSM), in the same time the total sulphide of control treatment decreased 10.7 mg/L (LSM). Two reasons existed which might cause the more decrease of free sulphide than total sulphide. Zinc acetate, which can be used to stabilize the sulphides by forming a ZnS precipitate, was used for the analysis of total sulphide during the dilution step, but can not be used for free sulphide analysis. A loss of free sulphide might occur when sample was poured into the instrument sampling tube after dilution. Another reason which contributes to the loss of free sulphide is the conversion of S^{2-} to sulphate (SO_4^{2-}) during analysis process. An antioxidant which is added as sample preservative in the dilution step can decrease this problem, but it can not be used with the free sulphide analysis method. It can only be used for the total sulphide analysis (George, 1993).

The concentration of total sulphide for voltage treatment at 0 and 168 h were 65.8 and 45 mg/L, respectively. The final concentration was 68.4% of the initial concentration. The decrease was considered to be due to the non-homogeneous nature of the samples and the release of $H_2S_{(g)}$ as mentioned before.

The concentration of total sulphide in the control treatment was 88.9 mg/L at 0 h, and 76.6 mg/L after 168 h of fermentation. The final concentration was 13.7% less than the initial concentration and was considered to be mainly due to the release of $H_2S_{(g)}$.

At time 0 h, 80% of total sulphide was free sulphide. After treatment, only 2.3% and 60% of total sulphide were present as free sulphide for voltage and control treatment, respectively.

There are several factors which may cause loss of sulphide during both free and total sulphide analysis process. There was no leakage on the Hungate tubes with butyl rubber septa before and after use, but there was a small loss which occurred as the needle was inserted and withdrawn from the sampling tube. There was also a small loss of gas when the sample was transferred into the solutions during dilution. Another factor was the oxidation which converted S^{2-} to SO_4^{2-} during storage. The amount of oxidation depends on the storage temperature, storage time and the amount of oxygen present in the tube (George, 1993). This amount of loss can be corrected by the following equation (Smith, 1993):

$$C_o = k * C_s$$

where: C_o is the real concentration of sulphide,

C_s is the concentration of sulphide after storage,

k is constant.

Constant k can be calculated by analyzing the sample right after sampling and after storage. In this experiment, because the workload and technical difficulties with the instrument, the storage time between sampling and analysis varied to differing degrees, it was impossible to correct them use above method.

It was also impossible to find the relationship between free sulphide and H_2S production rate because of the gas sampling method.

6.2 Gas phase

The H_2S data for the gas phase are listed in Appendix B. Five values were missing due to insufficient volume of samples collected in the gas bags.

The initial concentration of H_2S ranged between 1177 and 16024 ppm in the first run, between 1141 and 13906 ppm in the second run, between 437 and 10312 ppm in the third run, and 1764 and 15495 ppm in the final run. The variation in H_2S concentration of barrels was significant ($p<0.05$). In the experiment carried out by Yu et al. (1991), fresh manure was added to the barrels every second day. The H_2S production rates were found to be similar. In this experiment, manure was pumped into the bioreactors from a collection pit. It was possible that the solid contents varied between bioreactors even though thorough mixing was attempted. This appeared to be the major reason for the discrepancy.

Table 6.6 Analysis of covariance (H_2S)

Time (h)	TT	BK	TT*BK	HS0
24	*	***	**	**
168	***	=	=	=

*** significant at 0.001 level of probability
** significant at 0.01 level of probability
* significant at 0.05 level of probability
= not significant

The concentrations of H_2S were subject to analysis of covariance with the sources of variance of: blocks (BK), treatments (TT), treatment*block (TT*BK) and covariate (HS0) using the GLM procedure of SAS (1988).

Table 6.7 Concentrations of H_2S (ppm)[1]

Treatment	Time (h)	
	24	168
Control	9199 ± 1067^{a}	14044 ± 1546^{a}
1.5 V	4867 ± 1024^{b}	4234 ± 1241^{b}
2.0 V	5085 ± 1065^{b}	2171 ± 1330^{bc}
2.5 V	5874 ± 1031^{b}	151 ± 1375^{c}
3.0 V	3868 ± 1294^{b}	-298 ± 1399^{c}
3.5 V	6033 ± 1022^{b}	112 ± 1374^{c}

[1] Least square means(LSM), and standard errors of LSM.
[a,b,c] Means in the same column with a different superscript differ at $p<0.05$.

The results of analysis of covariance of H_2S concentration are presented in Table 6.6. In the gas phase, treatment effect was significant at 24 h and 168 h at levels of $p<0.05$ and $P<0.001$, respectively. Block effect was significant at 24 h at $p<0.001$ level, but not significant at 168 h. Covariate HS0 was significant at 0.5 h. The LSM concentrations of H_2S shown in Table 6.7 and Figure 6.3. Fisher's LSD procedure was employed to make pairwise comparisons among the treatment means (Table 6.7). At time 24 h and 168 h, control treatment had a significantly higher

concentration than all voltage treatments. The 1.5 V treatment had a significantly higher concentration than 2.5, 3.0, 3.5 V treatments at time 168 h. No significant difference was observed among the 2.0, 2.5, 3.0 and 3.5 V treatments.

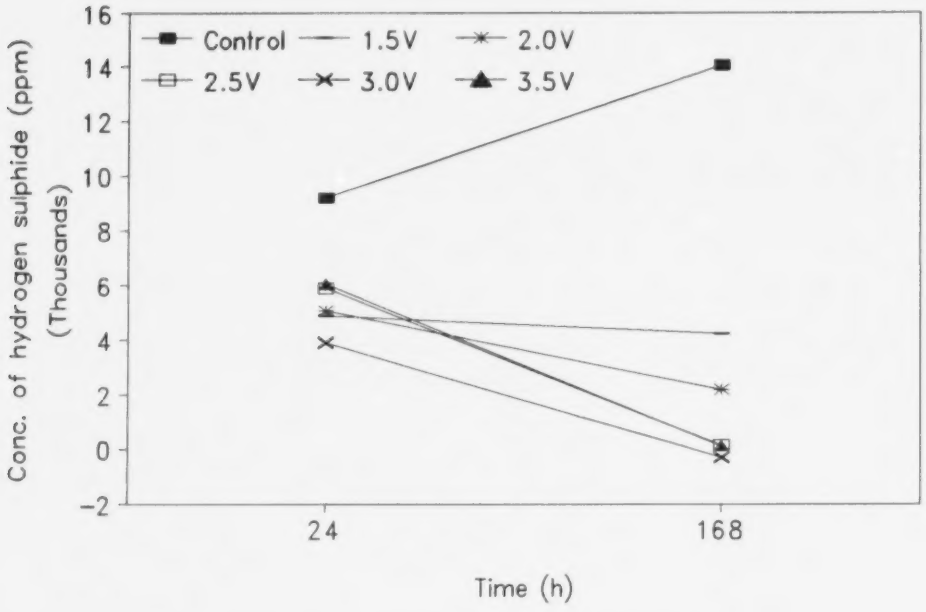


Figure 6.3 Concentrations of H_2S (LSM)

Gas samples obtained at 168 h were the accumulation of gas released from bioreactors in the final 6 days of treatment. Consequently, the concentrations of H_2S at 168 h were the average concentration of final 6 days. The mean concentrations of H_2S for the voltage treatments at 24 and 168 h were 5146 and 1274 ppm, respectively. The rate of H_2S removal was approximately 27 mg/L per hour. For the control, the concentration of H_2S increased with time with LSM of 9199 and 14044

ppm for 24 and 168 h, respectively. The mean concentration of H_2S for the voltage treatments over the final 6 days was 91% lower than the control. That is, the oligolysis with voltages ranging between 1.5 and 3.5 V resulted in a 91% reduction in the H_2S concentration in the gas released from stored pig manure.

6.3 Overall treatment effect

In order to see the overall treatment effect, sampling time was considered as another factor. The concentration of free sulphide, total sulphide and H_2S were subject to analysis of covariance individually based on the following linear model:

$$Y_{ijkl} = u + TT_i + BK_j + TT*BK_{ij} + BA(TT*BK)_{k(ij)} + T_l + TT*T_{il} + bS0_{ijkl} + E_{ijkl}$$

Where Y_{ijkl} is the ijklth observation of concentration; u is the population mean; TT_i is the fixed effect of treatments; BK_j is the random effect of experimental blocks; $TT*BK_{ij}$ is the interaction effect of treatment i and block j; $BA(TT*BK)_{k(ij)}$ is the random effect of barrels nested in block and treatment interaction; T_l is the fixed effect of sample times; $TT*T_{il}$ is the interaction effect of treatment i and time l; $S0_{ijkl}$ is the covariate (FS0 for free sulphide; TS0 for total sulphide and HS0 for hydrogen sulphide); b is the regression coefficient of Y_{ijkl} on $S0_{ijkl}$; E_{ijkl} is the random experimental error. $BA(TT*BK)_{k(ij)}$ is considered as the valid error for treatment TT_i.

6.3.1 Liquid phase

The results of analysis of covariance on free and total sulphide are tabulated in Table 6.8. Overall, treatment effect was significant at $p<0.001$ level for free sulphide and significant at $p<0.01$ level for total sulphide. The same results were obtained for block. Time was significant for both free and total sulphide at $p<0.001$ level.

Table 6.8 Analysis of covariance (Overall treatment effect on liquid phase)

Source	Free Sulphide	Total Sulphide
TT	***	**
BK	***	**
TT*BK	*	*
BA(TT*BK)	=	=
TIME	***	***
TT*TIME	=	=
SO	=	=

*** significant at 0.001 level of probability
** significant at 0.01 level of probability
* significant at 0.05 level of probability
= not significant

The treatment effects on free and total sulphide (LSM) are listed in Table 6.9 and shown graphically in Fig. 6.4. For free sulphide, orthogonal contrast with the treatment control versus other treatment levels revealed the other treatments had significantly lower concentration than the treatment control. No significant

Table 6.9 Concentration of sulphide (mg/L)[1] (Overall treatment effect on liquid phase)

Treatment	Free sulphide	Total sulphide
Control	64.7±2.9	82.0±4.8
1.5 V	37.6±2.1	52.7±3.3
2.0 V	39.5±2.6	53.7±3.7
2.5 V	38.2±2.0	60.9±3.4
3.0 V	35.9±2.3	57.1±3.9
3.5 V	29.5±2.0	56.7±3.3

[1] Least square means(LSM), and standard errors of LSM.

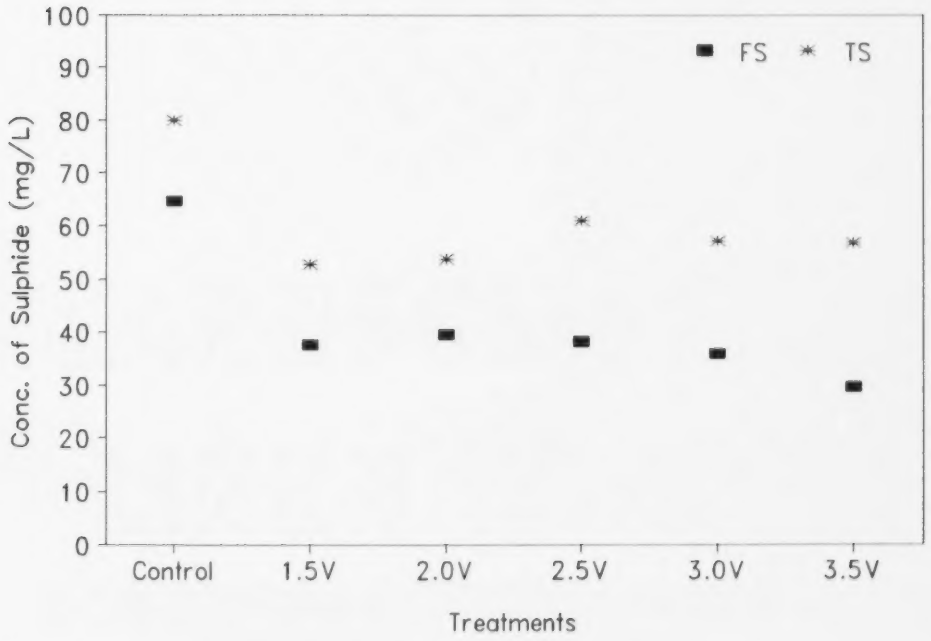


Figure 6.4 Overall treatment effect on free and total sulphide (LSM)

difference was observed among different voltage levels. The same results were obtained for total sulphide.

6.3.2 Gas phase

The results of analysis of covariance are presented in Table 6.10. Treatment effect was significant at $p<0.001$ level. Block and time were both significant at $p<0.01$ level. The treatment effect on H_2S (LSM) is listed in Table 6.11 and also shown graphically in Fig 6.5.

Table 6.10 Analysis of covariance (Overall treatment effect on gas phase)

Source	H_2S
TT	***
BK	**
TT*BK	**
BA(TT*BK)	=
TIME	**
TT*TIME	**
SO	=

*** significant at 0.001 level of probability
** significant at 0.01 level of probability
* significant at 0.05 level of probability
= not significant

Orthogonal contrast showed that there was a difference ($p<0.001$) between control treatment and voltage treatments, but no difference ($p>0.05$) among different voltage levels although the 3.0 V treatment had the lowest concentration value.

Table 6.11 Concentrations of H_2S (ppm)[1]
(Overall treatment effect on gas phase)

Treatment	H_2S
Control	11268 ± 1062
1.5 V	4440 ± 1018
2.0 V	3416 ± 1055
2.5 V	3684 ± 1024
3.0 V	1947 ± 1158
3.5 V	3321 ± 1017

[1] Least square means(LSM), and standard errors of LSM.

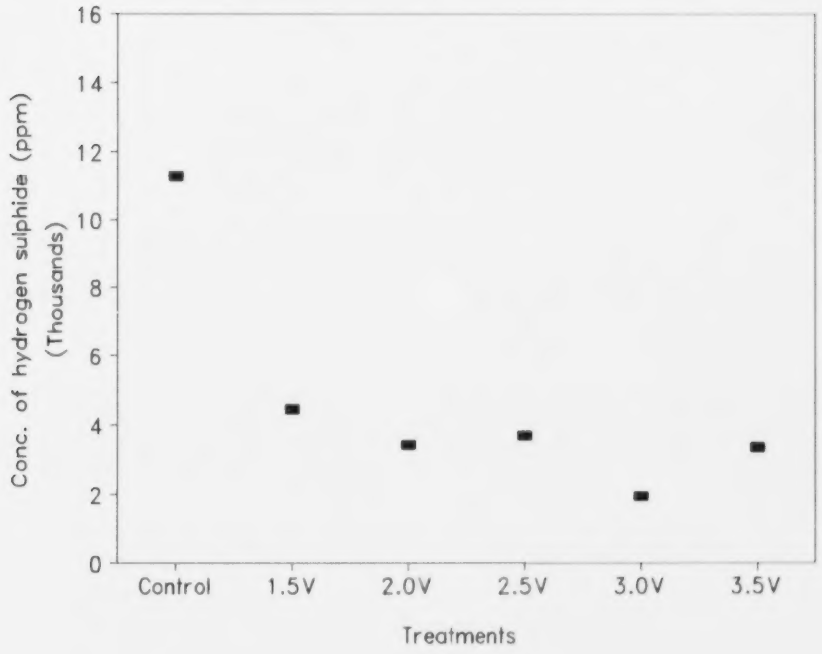


Figure 6.5 Overall treatment effect on H_2S (LSM)

Although no overall significant difference in free sulphide concentration was observed between voltage levels of 1.5, 2.0, 2.5, 3.0 and 3.5 V, the concentration of free sulphide after 168 h of treatment level 1.5 V was significantly higher than forvoltage levels of 3.0 and 3.5 V. The concentration of H_2S after 168 h of treatment level 1.5 V was significantly higher than treatment 2.5, 3.0 and 3.5 V. No significant difference was observed between the other four voltage levels. This may implied that 1.5 V may not enough to effectively remove free sulphide and H_2S from these bioreactors. In conclusion, 2 V appeared the optimum of oligolysis treatment for these bioreactors.

6.4 pH value

Sulphide in stored pig manure exists according to the following equilibrium equations:

$$H_2S_{(g)} \rightleftharpoons H_2S_{(aq)}$$

$$H_2S_{(aq)} \rightleftharpoons H^+ + HS^-$$

$$HS^- \rightleftharpoons H^+ + S^{2-}$$

These equations are pH dependent. Figure 6.6 shows the effect of pH on the sulphide equilibria. At pH less than 7, H_2S predominates. The HS^- dominates between pH 7 and 9.5 and the S^{2-} is predominant above pH 9.5.

Theoretically, with the release of every two Fe^{2+} ions from the anode, there will be one OH^- ion remaining in the slurry. That means that the pH value of manure will increase as treatment progresses. The rate of change will depend on

both voltage levels and treatment time. An increase in pH value will result in the reactions displacing to the right of the equations.

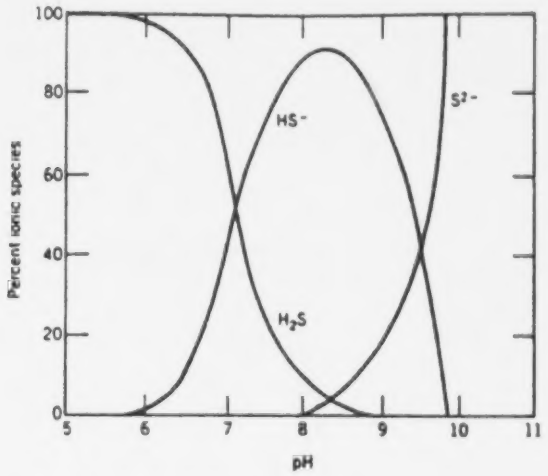


Figure 6.6 Forms of sulphides as a function of pH

(Adapted from Sawyer and McCarty, 1978)

The pH value data are listed in Appendix C. The mean pH value of liquid samples was in the alkaline range.

The pH data were subjected to an analysis of covariance based on the following linear model:

$$Y_{ijkl} = u + TT_i + BK_j + TT*BK_{ij} + BA(TT*BK)_{k(ij)} + T_l + TT*T_{il} + bPH0_{ijkl} + E_{ijkl}$$

Where Y_{ijkl} is the ijklth observation of concentration; u is the population

mean; TT_i is the fixed effect of treatments; BK_j is the random effect of experimental blocks; $TT*BK_{ij}$ is the interaction effect of treatment i and block j; $BA(TT*BK)_{k(ij)}$ is the random effect of barrels nested in block and treatment interaction; T_l is the fixed effect of sample times; $TT*T_{il}$ is the interaction effect of treatment i and time l; $PH0_{ijkl}$ is the covariate; b is regression coefficient of Y_{ijkl} on $PH0_{ijkl}$; E_{ijkl} is the random experimental error. $BA(TT*BK)_{k(ij)}$ was considered as the valid error for treatment TT_i. E_{ijkl} was the valid error for time T_k.

Table 6.12 Analysis of covariance (pH value)

Source	pH
TT	*
BK	***
TT*BK	=
BA(TT*BK)	=
TIME	***
TT*TIME	=
PHO	=

*** significant at 0.001 level of probability
** significant at 0.01 level of probability
* significant at 0.05 level of probability
= not significant

The results of analysis of covariance are summarized in Table 6.12. The treatment effect was significant at $p<0.05$ level. The LSM of pH value under different treatment levels are shown on Table 6.13. The pH value increased as voltage increased with the exception of the 2.0 V treatment. No reasons have been

found to explain this inconsistency. The time effect on the pH value was significant at $p<0.001$ level. The LSM of pH value for different sample time are listed in Table 6.14. The pH value of control and treated manure both increased with time. But the pH value of treated manure increased to 3% of the 0.5 h value whereas the pH value of control increased to 2% of the 0.5 h pH value.

Table 6.13 The treatment effect on pH value[1]

Treatment	pH
Control	7.14 ± 0.017^{a}
1.5 V	7.14 ± 0.016^{a}
2.0 V	7.20 ± 0.019^{b}
2.5 V	7.15 ± 0.016^{a}
3.0 V	7.19 ± 0.016^{b}
3.5 V	7.21 ± 0.016^{b}

[1] Least square means(LSM), and standard errors of LSM.
[a,b] Means in the same column with a different superscript differ at $p<0.05$.

Table 6.14 The time effect on pH value[1]

Time (h)	pH	
	Control	Treated
0.5	7.08 ± 0.03^{a}	7.11 ± 0.018^{a}
3	7.08 ± 0.04^{a}	7.12 ± 0.022^{a}
24	7.11 ± 0.03^{a}	7.15 ± 0.018^{a}
168	7.22 ± 0.04^{b}	7.33 ± 0.018^{b}

[1] Least square means(LSM), and standard errors of LSM.
[a,b] Means in the same column with a different superscript differ at $p<0.05$.

6.5 Gas production

Gas production volumes were monitored during the experiment. The gas production rate data are summarized in Appendix D. Gas production ranged from 0 to 23.7 mL/day /litre of manure. The average production rate was much lower than the results reported by Yu (1989). He reported that 202 mL/day /litre of manure gas was produced during treatment with oligolysis. Two possibilities exist to explain this discrepancy:

1. The pig manure was stored in the collection pit for at least three weeks prior to pumping to bioreactors. During this storage time some gases may have already been released to the atmosphere. In the experiment carried out by Yu (1989), manure collected was fresh and was added to the bioreactor every other day. This may have been responsible for the higher gas production rates in his experiment.

2. Tchobanoglous and Burton (1991) noted that the equilibrium or saturation concentration of gas dissolved in a liquid is a function of the type of gas and the partial pressure of the gas adjacent to the liquid. The relationship between the partial pressure of the gas in the atmosphere above the liquid and the concentration of the gas in the liquid is governed by Henry's law:

$$P_g = H^* X_g$$

where: P_g = partial pressure of gas, atm

H = Henry's law constant, atm/mol fraction

$$X_g = \text{equilibrium mole fraction of dissolved gas}$$

$$= \frac{\text{mol gas } (n_g)}{\text{mol gas } (n_g) + \text{mol water } (n_w)}$$

Henry's law constant is a function of the type, temperature and constituents of the liquid. For a certain kind of gas, if the temperature is constant H is constant. The gas compounds in a mixture react independently from each other. According to this X_g is directly proportional to P_g. i.e.,:

$$\frac{n_g}{n_g + n_w} = \frac{P_g}{H}$$

Since $n_g * P_g/H$ is much less than n_g, n_g is approximately equal to $P_g * n_w / H$. That is the saturation concentration of a gas is proportional to its partial pressure P_g.

According Dalton's law of partial pressure, if two or more different gases that do not interact chemically are present in a container, their partial pressures contribute independently to the total pressure.

In this experiment the temperature of the manure was kept constant and the bioreactors were completely sealed. When gas was released to the head space of bioreactor above manure, the total partial pressure of P_g would increase and therefore, the saturation concentration of different gases in liquid would increase. This would result in the gas released to the head space of the manure being reduced.

6.6 Iron consumption

The mass of the cathodes was unchanged for all bioreactors in all runs. The mass loss of anodes for each run is tabulated in Appendix F and the mean mass loss of anodes is listed in Table 6.15.

Table 6.15 Mean mass loss of anodes

Volts	g/day	g/volt/day	g/mm^2/day*
1.5	5.4	3.6	1.2×10^{-4}
2.0	6.8	3.4	1.5×10^{-4}
2.5	9.6	3.8	2.1×10^{-4}
3.0	19	6.3	4.1×10^{-4}
3.5	15.2	4.3	3.3×10^{-4}

* g per mm^2 of surface area of anode

The mass loss of anodes was proportional to the amount of current that flowed in the bioreactor. Theoretical calculation indicated that 1.03 grams of iron will be released per amp-hr of current flowing across the bioreactor (Feddes and Coleman 1993; Snoeyink and Jenkin, 1980). According to Ohm's Law, the greater the voltage applied, the greater will be the amount of current carried if the resistance remains constant. Therefore the greater the voltage applied, the greater the amount of mass loss. The results of this experiment were generally in accordance with the above observation with the exception of a larger than expected mass loss at 3.0 V. No reason was apparent to explain this discrepancy. It was also noticed that treatment level 3.0 V, which had the highest mass loss, also had the lowest final

concentration of free and total sulphide and the lowest final concentration of H_2S. Mass loss expressed as g/volt ranged between 23.8 and 30.4 with the exception of treatment 3.0 V which lost 44.3 g/volt. If mass loss was presented as grams per mm^2 of surface area of anode, it ranged from 8.23×10^{-4} to 2.89×10^{-3} g/mm^2.

6.7 Current in the experiment

The current level was allowed to fluctuate freely in the experiment under constant voltage levels. It was observed that the current level in the experiment exhibited a significant variation with time. However, a consistent pattern developed in that the current level was highest when the experiment was initiated. Then it decreased quickly with time. After 24 h, the current stabilized, although the current level at 168 h was the lowest for each bioreactor. The reason for this was that, at the beginning of the experiment, the iron bars were clean. As the treatment progressed, more and more FeS were formed. The two iron bars were coated with a black film of thin material. This coating appeared to significantly increase the resistance between the two iron bars and at the same time reduce the current level. If the electrodes can be cleaned during the treatment process, the efficiency of the oligolysis treatment can be increased. One of approach was considered to alternating the polarity of the electrodes. The frequency of switching was considered before the electrodes were fully coated. This is the area need further research.

The mean current level of treated bioreactors in the whole experiment was 0.3 A. The average voltage level was 2.5 V. The energy consumption was 0.56

kwh/m^3 for 7 days treatment. The energy consumption can be lowered by reducing the treatment voltage level and by reducing the treatment time. If 2.0 V was used for these bioreactors, the energy consumption will be less than 0.45 kwh/m^3. Since samples were not taken between 24 h and 168 h, there was a possibility that the free sulphide and H_2S had been removed before 168 h. If the treatment time can be reduced, the energy consumption can significantly be reduced.

6.8 T.O.N.

The T.O.N. was calculated as the geometric mean of thresholds of individual on the panels. The original data of T.O.N. are listed in Appendix F. The means of T.O.N. are listed in Table 6.16.

Table 6.16 Means of T.O.N.

Treatment	T.O.N.
Control	151212
1.5 V	128268
2.0 V	154986
2.5 V	159867
3.0 V	115032
3.5 V	110065

The data were subject to analysis of variance (SAS, 1988). The results showed that the treatment effect was insignificant ($p > 0.05$).

Although free sulphide was almost completely removed from the treated manure, no difference in T.O.N. was noticed between treated samples and control

samples on T.O.N. This may imply that the free sulphide is not the indicator of smell of pig manure. Other compounds other than free sulphide appear to be more responsible for the odour of stored pig manure.

These results agree with these presented by Spoelstra (1980), where he indicated that H_2S and NH_3 do not seem very suitable as indicators of smell.

Tchobanoglous and Burton (1991) also note that although H_2S is the most important gas formed from the standpoint of odour, other volatile compounds such as indole, skatol, and mercaptans, which may also be formed during anaerobic decomposition, may cause odour far more offensive than that of H_2S.

Smelling the odour from the undiluted treated manure and the untreated manure indicated a stronger smell in the untreated manure compared to the treated manure. But with the dilution of up to about 10000, the difference could not be detected. The dilutions of samples were between 2.5 and 28.5 ppm for T.O.N. test. Since the dilution ratio was so high, the odour characteristics may have changed.

Because the smell of odour from the manure storage by the neighbours is the dilute concentration of the odour source, the T.O.N. test appeared more reliable than smelling the original sample for detecting odour reduction. In this case, oligolysis may not be effective for reducing the odour from stored pig manure.

6.9 General observations

After each trial run, the anode was visibly corroded, while deposits collected on the cathode with no weight loss. When the barrels were emptied at the end of

the test it was observed that a blackish slime had settled at the bottom of treated manure bioreactors.

7. CONCLUSIONS

The following conclusions are drawn from this study:

1. Oligolysis treatment removed 98% of free sulphide from the liquid phase of pig manure and reduced the concentration of hydrogen sulphide released from the stored pig manure by 91%. This suggests that oligolysis treatment is an effective method to reduce H_2S production, therefore reduce the health hazards from the release of acutely toxic levels of H_2S.

2. No significant difference on the effectiveness of oligolysis treatment was observed among applied voltages of 1.5, 2.0, 2.5, 3.0 and 3.5 V on the removal of free sulphide and H_2S.

3. Although free sulphide was almost completely removed from treated manure, no significant difference in T.O.N. was observed between different treatment levels. This implied that oligolysis treatment for odour control may not be effective since odours reach neighbours in very dilute concentrations.

4. Two volts appeared the optimum to effectively remove free sulphide and H_2S from these bioreactors.

5. The rate of H_2S removal was 27 mg/L/h.

6. Energy comsuption was 0.56 kwh/m^3.

7. Iron consumption rate was 3.4 to 6.3 g/volt/day or 1.2×10^{-4} to 4.1×10^{-4} g/mm^2/day surface area of anode.

8. RECOMMENDATIONS

1. If the same experiment is repeated, at least two more sampling times are recommended during the 24 to 168 h period.

2. The gas sampling method needs improvement due to the low gas production rate.

3. An economical analysis is recommended to determine the feasibility of this treatment method.

4. Alternating the polarity of the electrodes should be investigated to reduce the effect of crusting.

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APPENDIX A : CONCENTRATIONS OF FREE SULPHIDE AND TOTAL SULPHIDE (mg/L)

Treatment	Block	FS 0h	TS 0h	FS 0.5h	TS 0.5h	FS 3h	TS3h	FS 24h	TS 24h	FS 168h	TS 168h
Control	1	91.0	91.5	116.5	.	86.5	73.6	57.8	53.6	60.4	78.3
Control	1	67.7	74.6	84.7	.	89.0	75.7	68.9	54.6	48.6	87.3
1.5 V	1	41.2	51.4	85.9	.	86.5	60.9	40.0	54.6	0.0	50.1
1.5 V	1	54.5	67.3	79.8	.	47.3	35.6	41.2	59.9	0.0	33.2
2.0 V	1	35.1	52.5	122.0	.	92.6	28.2	36.6	57.8	2.5	51.2
2.0 V	1	50.0	81.0	96.9	.	104.3	97.8	33.8	56.7	0.0	60.2
2.5 V	1	51.1	55.7	81.6	.	73.0	75.7	32.8	59.9	0.0	50.1
2.5 V	1	77.2	86.2	73.6	.	55.9	40.9	42.8	63.0	0.0	62.5
3.0 V	1	48.4	54.6	93.2	.	81.6	72.5	20.1	57.8	0.0	.
3.0 V	1	61.1	91.5	77.3	.	43.6	53.6	29.0	101.0	0.0	35.5
3.5 V	1	72.2	51.4	18.5	.	51.2	38.8	0.0	59.9	0.0	51.2
3.5 V	1	63.3	52.5	82.8	.	36.3	70.4	13.1	56.7	0.0	53.5
Control	2	55.9	73.0	48.5	61.4	60.8	71.8	40.7	49.9	34.9	71.8
Control	2	57.8	79.9	54.9	69.5	54.9	62.6	37.2	46.5	40.7	73.4
1.5 V	2	39.2	48.8	33.8	46.5	31.8	48.8	11.2	52.2	0.0	39.2
1.5 V	2	44.6	48.8	36.2	50.0	28.9	47.6	14.6	43.0	0.0	57.3
2.0 V	2	39.2	48.8	33.8	41.9	44.6	55.7	14.6	40.7	2.5	53.3
2.0 V	2	39.7	40.7	26.9	40.7	39.7	54.5	18.6	43.0	0.0	63.3
2.5 V	2	38.7	47.6	32.8	47.6	42.1	52.2	15.1	45.3	0.0	41.2
2.5 V	2	43.6	53.3	47.5	56.8	45.1	61.4	18.6	52.2	0.0	54.3
3.0 V	2	.	.	36.2	55.7	36.2	53.4	11.2	50.0	0.0	53.3
3.0 V	2	55.4	67.2	44.6	59.1	40.7	61.4	12.7	47.6	0.0	42.2
3.5 V	2	58.3	53.3	51.0	54.5	32.8	54.5	0.0	35.0	0.0	49.2
3.5 V	2	36.2	48.8	33.8	45.3	31.8	50.0	9.2	41.9	0.0	48.2

Control	3	77.4	86.2	64.7	120.7	72.9	116.6	79.2	133.3	46.3	82.4
Control	3	86.9	128.1	81.9	104.0	68.4	110.3	81.9	156.3	44.6	67.0
1.5 V	3	70.7	68.5	70.1	61.6	65.4	83.5	52.1	61.6	15.1	36.2
1.5 V	3	59.8	87.0	57.6	62.7	58.9	107.8	52.5	46.6	5.2	28.5
2.0 V	3	52.1	53.5	64.1	62.7	54.6	98.5	40.6	66.2	0.0	19.3
2.0 V	3	48.6	46.6	55.1	51.2	41.9	51.2	47.9	58.1	0.0	23.9
2.5 V	3	66.6	47.5	61.9	78.9	62.4	107.1	53.4	92.5	2.8	60.9
2.5 V	3	73.1	61.1	75.7	67.4	60.6	83.1	35.7	61.1	1.2	31.6
3.0 V	3	64.1	92.7	59.8	75.4	60.2	67.4	52.1	46.6	0.0	43.9
3.0 V	3	63.6	78.9	56.8	38.5	57.6	59.3	33.2	59.3	0.0	42.4
3.5 V	3	60.6	90.4	61.5	61.1	56.4	83.1	47.6	82.0	0.0	34.7
3.5 V	3	58.8	74.2	59.3	71.5	61.6	92.5	57.5	88.8	1.8	30.1

. - Missing data
FS - Free sulphide
TS - Total sulphide

APPENDIX B: CONCENTRATIONS OF HYDROGEN SULPHIDE (ppm)

Treatment	Block	0 h	24 h	168 h
Control	1	1498	3462	.
Control	1	15181	9731	14489
1.5 V	1	6403	7855	523
1.5 V	1	15037	12258	7847
2.0 V	1	14275	13132	10014
2.0 V	1	2820	13573	74.50
2.5 V	1	1177	8390	.
2.5 V	1	16024	18975	160
3.0 V	1	.	3404	1.57
3.0 V	1	14182	11737	536
3.5 V	1	12590	15528	4.25
3.5 V	1	10850	11498	378
Control	2	13906	9426	14791
Control	2	12670	3144	6640
1.5 V	2	1141	1292	16.46
1.5 V	2	1780	656	1.47
2.0 V	2	10428	244	2.38
2.0 V	2	3109	290	7.89
2.5 V	2	3321	506	3.42
2.5 V	2	9718	1929	15.64
3.0 V	2	11389	546	15.72
3.0 V	2	4441	.	12.63
3.5 V	2	11697	1418	13.96
3.5 V	2	1634	1280	16.04
Control	3	4289	4262	9391
Control	3	5505	11542	16705
1.5 V	3	10312	9523	8924
1.5 V	3	4589	1330	8.54
2.0 V	3	1376	1184	2.6
2.0 V	3	437	459	2.1
2.5 V	3	3733	1090	122
2.5 V	3	3397	1932	14.2
3.0 V	3	6064	3735	35
3.0 V	3	890	4574	30
3.5 V	3	903	4575	.
3.5 V	3	3023	6074	341
Control	4	12284	14103	18353
Control	4	14110	25716	27231

1.5 V	4	5876	3112	11958
1.5 V	4	9570	1004	2139
2.0 V	4	6097	3308	3.02
2.0 V	4	1764	930	244
2.5 V	4	6601	4442	1701
2.5 V	4	6838	6291	49.2
3.0 V	4	15276	4892	54.5
3.0 V	4	7385	1488	2.45
3.5 V	4	15495	5144	115
3.5 V	4	5920	3745	254

. - Missing data

APPENDIX C: THE PH VALUE OF LIQUID SAMPLES

Treatment	Block	0 h	0.5 h	3 h	24 h	168 h
Control	1	7.01	6.86	.	6.94	7.23
Control	1	7.03	6.90	.	6.93	7.22
1.5 V	1	7.22	7.02	.	7.03	7.38
1.5 V	1	7.17	6.95	.	7.02	7.33
2.0 V	1	7.20	7.02	.	7.01	7.39
2.0 V	1	7.19	7.03	.	6.99	7.39
2.5 V	1	7.22	6.93	.	7.03	7.41
2.5 V	1	7.11	6.96	.	6.98	7.41
3.0 V	1	7.13	6.95	.	7.03	7.61
3.0 V	1	7.13	6.86	.	6.92	7.33
3.5 V	1	7.13	6.97	.	7.01	7.61
3.5 V	1	7.16	6.99	.	7.03	7.56
Control	2	7.18	7.22	7.19	7.17	7.18
Control	2	7.25	7.21	7.19	7.23	.
1.5 V	2	7.05	7.06	7.07	7.10	7.05
1.5 V	2	7.16	7.13	7.16	7.27	7.25
2.0 V	2	7.23	7.26	7.26	7.35	7.39
2.0 V	2	7.26	7.26	7.25	7.38	7.38
2.5 V	2	7.12	7.18	7.16	7.12	7.22
2.5 V	2	7.24	7.16	7.15	7.17	7.30
3.0 V	2	7.17	7.22	7.18	7.32	7.40
3.0 V	2	7.24	7.23	7.18	7.29	7.43
3.5 V	2	7.16	7.20	7.21	7.22	7.36
3.5 V	2	7.15	7.19	7.16	7.18	7.28
Control	3	7.11	7.17	7.04	7.18	7.15
Control	3	7.14	7.12	7.13	7.20	7.17
1.5 V	3	7.12	7.13	7.07	7.19	7.10
1.5 V	3	7.12	7.12	7.05	7.15	7.17
2.0 V	3	7.22	7.28	7.12	7.30	7.33
2.0 V	3	7.21	7.25	7.16	7.29	7.21
2.5 V	3	7.19	7.20	7.18	7.19	7.30
2.5 V	3	7.13	7.03	7.03	7.12	7.20
3.0 V	3	7.11	7.13	7.08	7.19	7.28
3.0 V	3	7.21	7.15	7.08	7.25	7.32
3.5 V	3	7.13	7.19	7.14	7.19	7.19
3.5 V	3	7.09	7.19	7.14	7.22	7.20

. - Missing data

APPENDIX D: GAS PRODUCTION RATES (mL/L/day)

Treatment	Block	0 h	24 h	168 h
Control	1	1.7	*	-
Control	1	*	*	*
1.5 V	1	*	*	*
1.5 V	1	*	8.9	1.8
2.0 V	1	0.1	*	0.6
2.0 V	1	*	*	*
2.5 V	1	*	*	*
2.5 V	1	2.2	22.2	0.9
3.0 V	1	*	*	-
3.0 V	1	*	*	1.4
3.5 V	1	*	8.9	0.2
3.5 V	1	*	*	2.8
Control	2	0.5	*	-
Control	2	5.6	*	*
1.5 V	2	*	*	-
1.5 V	2	*	*	*
2.0 V	2	*	*	-
2.0 V	2	*	*	*
2.5 V	2	*	*	-
2.5 V	2	2.8	*	*
3.0 V	2	*	*	-
3.0 V	2	1.0	*	*
3.5 V	2	*	*	-
3.5 V	2	*	*	*
Control	3	0.6	*	-
Control	3	3.3	*	*
1.5 V	3	*	*	-
1.5 V	3	*	*	*
2.0 V	3	*	*	-
2.0 V	3	*	*	*
2.5 V	3	*	*	-
2.5 V	3	*	*	*
3.0 V	3	0.4	*	-
3.0 V	3	0.9	21.1	*
3.5 V	3	1.9	2.8	-
3.5 V	3	*	4.7	*
Control	4	1.7	*	-
Control	4	*	*	*

1.5 V	4	*	*	-
1.5 V	4	*	*	1.4
2.0 V	4	0.1	*	0.6
2.0 V	4	*	*	*
2.5 V	4	*	*	*
2.5 V	4	2.2	22.2	0.9
3.0 V	4	*	*	*
3.0 V	4	0.1	9.4	1.8
3.5 V	4	*	8.9	0.2
3.5 V	4	*	*	2.8

* - Below detectable level
- - Not available

APPENDIX E: MASS LOSS OF ANODES (g)

Treatment	Block 1	Block 2	Block 3
1.5 V	38.8	51.8	9.4
1.5 V	27.5	85.3	16.1
2.0 V	31.1	54.0	66.9
2.0 V	55.3	40.0	38.4
2.5 V	105.7	100.1	28.3
2.5 V	85.7	29.3	52.5
3.0 V	152.3	107.2	71.4
3.0 V	174.8	206.1	86.0
3.5 V	229.7	96.8	61.5
3.5 V	135.8	66.2	48.5

APPENDIX F: THRESHOLD ODOUR NUMBER

Treatment	Block 1	Block 2	Block 3	Block 4
Control	140000	168179	100000	199194
Control	140709	233315	99597	128705
1.5 V	99597	186229	75480	88194
1.5 V	80734	158740	99329	237841
2.0 V	106530	162122	157675	251984
2.0 V	62588	98995	200000	200000
2.5 V	125561	162122	200000	217551
2.5 V	108228	182938	153832	128705
3.0 V	150961	91008	177581	99329
3.0 V	131419	78837	65975	125146
3.5 V	70000	140000	151572	111869
3.5 V	141136	79370	61433	125146

APPENDIX G: SAS PROGRAMS

1. SAS PROGRAM FOR THE FREE AND TOTAL SULPHIDE ANALYSIS:

```
CMS FILEDEF ABC DISK TZ DATA A1;
DATA JOB1;
INFILE ABC MISSOVER FIRSTOBS=2;
INPUT TT & BK FS0 TS0 FS1 TS1 FS2 TS2 FS3 TS3 FS4 TS4;
PROC SORT;
BY TT;
PROC PRINT;
TITLE " LIQUID SULPHIDE";
PROC GLM;
CLASS TT BK;
MODEL FS1 FS2 FS3 FS4 = TT BK TT*BK FS0/SS3;
LSMEANS TT BK/STDERR PDIFF ETYPE=3;
PROC GLM;
CLASS TT BK;
MODEL TS1 TS2 TS3 TS4 = TT BK TT*BK TS0/SS3;
LSMEANS TT BK/STDERR PDIFF ETYPE=3;
PROC SORT;
BY TT;
```

2. SAS PROGRAM FOR HYDROGEN SULPHIDE ANALYSIS:

```
CMS FILEDEF ABC DISK THZ DATA A1;
DATA JOB 1;
INFILE ABC MISSOVER FIRSTOBS=2;
```

```
INPUT TT $ BK HS0 HS1 HS2;
PROC SORT;
BY TT;
PROC PRINT;
TITLE 'CONCENTRATION OF HYDROGEN SULPHIDE (PPM)'
PROC GLM;
CLASS TT BK;
MODEL HS1 HS2 = TT BK TT*BK HS0/SS3;
LSMEANS TT BK/STDERR PDIFF ETYPE=3;
PROC SORT;
BY TT;
```

3. SAS PROGRAM FOR OVERALL TREATMENT EFFECTS ON FREE AND TOTAL SULPHIDE:

1) FOR FREE SULPHIDE

```
CMS FILEDEF ABC DISK TZ DATA A1;
DATA JOB1;
INFILE ABC MISSOVER FIRSTOBS=2;
INPUT TT $ BK BA FS0 TS0 FS1 TS1 FS2 TS2 FS3 TS3 FS4 TS4;
FS=FS1;
TIME=1;
OUTPUT;
FS=FS2;
TIME=2;
OUTPUT;
FS=FS3;
```

```
TIME=3;
OUTPUT;
FS=FS4;
TIME=4;
OUTPUT;
PROC GLM DATA=JOB1;
CLASS BK TT TIME BA;
MODEL FS=BK TT BK*TT BA(BK*TT) TIME*TT FS0/SS1 SS3;
LEANS TT/E=BA(BK*TT) PDIFF STDERR;
LEMEANS TIME/PDIFF SEDERR;
TEST H=TT E=BA(BK*TT);
TITLE'TREATMENT EFFECTS ON FS';
PROC MEANS NOPRINT;
BY BK TT BA;
VAR FS0 TS0 FS;
OUTPUT OUT=AVGS MEAN=FS0MEAN TS0MEAN FSMEAN;
PROC PRINT;
TITLE 'AVERAGES COMPUTED OVER THE DIFFERENT TIMES';
PROC GLM;
CLASS BK TT;
MODEL FSMEAN=BK TT BK*TT FS0MEAN/SS1 SS3;
LSMEANS TT/PDIFF STERR;
* - TT - - -ORDER - - -          L1 L2 L3 L4 L5 L6;
CONTRAST 'L1 VS REST        'TT  5  -1 -1 -1  -1 -1;
CONTRAST 'L2 L3 VS L4 L5 L6 'TT  0   3  3 -2  -2 -2;
CONTRAST 'L2 VS L3          'TT  0   1 -1  0   0  0;
```

```
CONTRAST 'L4 VS L5 L6        TT  0   0  0  2  -1  -1;
CONTRAST 'L5 VS L6           TT  0   0  0  0   1  -1;
RUN;
```

2) FOR TOTAL SULPHIDE

SAS PROGRAM FOR OVERALL TREATMENT EFFECT ON TOTAL SULPHIDE IS SAME WITH FREE SULPHIDE WITH THE EXCEPTION OF TS INSTEAD OF FS.

4. SAS PROGRAM FOR OVERALL TREATMENT EFFECTS ON HYDROGEN SULPHIDE:

```
CMS FILEDEF ABC DISK THZ DATA A1;
DATA JOB1;
INFILE ABC MISSOVER FIRSTOBS=2;
INPUT TT $ BK BA HS0 HS1 HS2;
HS=HS1;
TIME=1;
OUTPUT;
HS=HS2;
TIME=2;
OUTPUT;
PROC GLM DATA=JOB1;
CLASS BK TT TIME BA;
MODEL HS=BK TT BK*TT BA(BK*TT) TIME TIME*TT HS0/SS1 SS3;
LSMEANS TT /E=BA(BK*TT) PDIFF STDERR;
TEST H=TT E=BA(BK*TT);
TITLE'TREATMENT EFFECTS ON HS';
PROC MEANS NOPRINT;
```

```
BY BK TT BA;
VAR HS0 HS;
OUTPUT OUT=AVGS MEAN=HS0MEAN HSMEAN;
PROC PRINT;
TITLE 'AVERAGES COMPUTED OVER THE DIFFERENT TIMES';
PROC GLM;
CLASS BK TT;
MODEL HSMEAN=BK TT BK*TT HS0MEAN/SS1 SS3;
LSMEANS TT/PDIFF STERR;
* - TT - - ORDOR - - - - - -      L1 L2 L3 L4 L5 L6;
CONTRAST ' L1 VS REST          'TT  5 -1 -1 -1 -1 -1;
CONTRAST ' L5 VS L2 L3 L4 L6 'TT  0 -1 -1 -1  4 -1;
RUN;
```

5. SAS PROGRAM FOR T.O.N. ANALYSIS:

```
CMS FILEDEF ABC DISK TON DATA A1;
DATA JOB1;
INFILE ABC MISSOVER FIRSTOBS=2;
INPUT TT $ BK TON;
PROC DORT;
BY TT;
PROC GLM;
CLASS TT BK;
MODEL TON= TT BK TT*BK;
MEANS TT BK;
RUN;
```

6. SAS PROGRAM FOR PH VALUE ANALYSIS

```
CMS FILEDEF ABC DISK PH DATA A1;
DATA JOB 1;
INFILE ABC MISSOVER FIRSTOBS=2;
INPUT TT $ BK PH0 PH1 PH2 PH3 PH4;
PROC SORT;
BY TT;
PROC PRINT;
TITLE 'PH VALUE'
PROC GLM;
CLASS TT BK;
MODEL PH1 PH2 PH3 PH4 = TT BK TT*BK PH0/SS3;
LSMEANS TT BK/STDERR PDIFF ETYPE=3;
PROC SORT;
BY TT;
```

7. OVERALL TREATMENT EFFECT ON PH VALUE

```
CMS FILEDEF ABC DISK PH DATA A1;
DATA JOB1;
INFILE ABC MISSOVER FIRSTOBS=2;
INPUT TT $ BK BA PH0 PH1 PH2 PH3 PH4;
PH=PH1;
TIME=1;
OUTPUT;
PH=PH2;
TIME=2;
```

```
OUTPUT;
PH=PH3;
TIME=3;
OUTPUT;
PH=PH4;
TIME=4;
OUTPUT;
PROC GLM DATA=JOB1;
CLASS BK TT TIME BA;
MODEL PH=BK TT BK*TT BA(BK*TT) TIME*TT PH0/SS1 SS3;
LEANS TT/E=BA(BK*TT) PDIFF STDERR;
LEMEANS TIME/PDIFF SEDERR;
TEST H=TT E=BA(BK*TT);
TITLE'TREATMENT EFFECTS ON PH';
PROC MEANS NOPRINT;
BY BK TT BA;
VAR PH0 PH;
OUTPUT OUT=AVGS MEAN=PH0MEAN FSMEAN;
PROC PRINT;
TITLE 'AVERAGES COMPUTED OVER THE DIFFERENT TIMES';
PROC GLM;
CLASS BK TT;
MODEL PHMEAN=BK TT BK*TT PH0MEAN/SS1 SS3;
LSMEANS TT/PDIFF STERR;
```